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# DEVELOPMENT OF CONSERVATION METHODS FOR THE RESTORATION OF PAPER MATERIALS

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## *Presentation*

Paper, one of the most common materials of Cultural Heritage, undergoes serious deterioration caused by physical, chemical and biological factors. One of the main causes of deterioration is the acidic and/or oxidative environment.

The studies of deterioration and conservation of paper have been increasing and require further development of methods and treatments that can stabilize and strengthen the paper. Various conservation treatments are being applied to model and to historical paper by using different chemicals methods. Their effectiveness for conservation and restoration are under study.

Internal and external factors degrade the paper by promoting various reaction pathways. The two most important classes of reactions are acid hydrolysis that shortens the cellulose polymeric chains thus weakening the mechanical properties of the paper, and oxidation with subsequent development of chromophores that cause discoloration of the remaining substratum and other byproducts.

The effort of researchers as well as that of restorers has been mainly focused to the problem of paper acidity.

For stabilizing and preventing acidic paper degradation, alkaline compounds are used in order to neutralize the acidic agents and to form deposit of alkaline reserve.

Nanolime dispersions for the deacidification of ancient paper constitute a valid alternative to the lime traditional ones. Its efficacy depends on particles size, polydispersity and agglomeration that can be controlled depending on the preparation method. Different researches[1,2] showed that nanolime particles dispersed in aqueous and alcoholic media can be applicable to paper conservation giving rise to good results.

Up to now the problem of oxidation is neglected. Only a limited number of reducing agent can be used on degraded paper without damaging the fibers structure and the inks. Several researchers from different areas showed the efficiency of tert-butyl amine borane complex (TBAB) as a reducing agent for paper conservation. TBAB has been experimented by researchers from “Istituto

[1] Sequeira, S., Casanova, C., Cabrita, E. J.. "Deacidification of paper using dispersions of Ca (OH) 2 nanoparticles in isopropanol. Study of efficiency."Journal of Cultural Heritage 7.4 (2006): 264-272.
[2] Poggi, G., et al. "Hydroxide nanoparticles for deacidification and concomitant inhibition of iron-gall ink corrosion of paper." Langmuir 26.24 (2010): 19084-19090.

Centrale per la Patologia del Libro" (ICPL) of Rome and its use is accepted by restaurateurs as reducing agent for the carbonyl groups.

During the PhD research activity, with the aim to study conservative problems of paper, a new method for nanolime preparation by insolubilisation-precipitation has been devised. Nanoparticles dispersed in a water/2-propanol mixture were obtained without any manipulation of the dispersion. The stability of the dispersion together with particle size and morphology were found to be dependent on water to 2-propanol molar ratio and on the synthesis temperature. One of the prepared dispersion was applied on two manuscripts to assess its efficiency.

Further, an innovative treatment based on nanolime and TBAB for the simultaneous deacidification and reduction of ancient paper was set and applied on model and ancient papers. Physical chemical characterization showed that the samples subjected to the proposed treatment improve their mechanical and optical properties as a consequence of their state of oxidation, acidity and degree of polymerization.

The thesis is divided into two parts. In the first part, an overview of the causes and the mechanisms of paper degradation and of the characterization methodologies is presented. The second part is structured in three chapters: in the first the deacidification of paper is treated. The new synthesis methodology of calcium hydroxide nanoparticles is presented and the evaluation of its efficiency is discussed. In the second chapter the innovative treatment for the simultaneous deacidification and reduction is presented. Its efficacy on specimens of cellulose paper, unwritten and written with iron gall ink, and of lignin paper is discussed. In the third chapter the above systems are applied on three case studies. The appendix reports the characterization methods utilized during the research activity.

# *FIRST PART*

# *CHAPTER I*

# *PAPER: CAUSES AND MECHANISMS OF ITS DEGRADATION*

## 1.1 Composition of paper

The paper is a substrate of a complex multi-component mixture of cellulose, hemicellulose and lignin with other chemical compounds (fillers, additives, sizing and others)[3,4]. Different causes of degradation such as mechanical, chemical, physical and biological produces undesirable characteristics on the paper.

Understanding the history, use, structure, chemical composition, causes of degradation, degradation mechanism, chemical process involved in paper making and paper degradation are helpful for overcoming the conservation challenges of inhibiting further degradation and for choosing the appropriate conservation treatments and methods.

Paper production[5] originated in China at the beginning of the II century B.C. In Europe paper was brought by Arabs. It was introduced in Spain in the IX century. The chronology of its diffusion across Europe is: X century in France (Essonnes) and in Italy (Amalfi, Fabriano), XIV century in Germany and at the end of the XV century in England.

The Chinese production was based on the use of various types of vegetable as raw materials. Arabs introduced the use of linen and cotton rags whose use as basic raw material persisted until the last century. The invention of the paper machine, in 1797 in France, led to a raise of paper production with the contemporary request of raw materials. The result was the need to find a more affordable material than rags thus industries turned to the wood pulp. Because the alone mechanical treatment of wood did not produce very good quality pulp or paper, chemical processes were developed to

[3] May, E. and Jones, M. Conservation science: heritage materials. Royal Society of Chemistry, 2006.
[4] Artioli, G. Scientific methods and cultural heritage: an introduction to the application of materials science to archaeometry and conservation science. Oxford University Press, 2010.
[5] Erhardt, D., and Tumosa, C. S. "Chemical degradation of cellulose in paper over 500 years." Restaurator 26.3 (2005): 151-158.

remove some of the non-cellulosic components such as lignin and colored materials. The technological process of making paper fibers changed with the introduction of new raw materials. New chemical and physical pulping processes and the adoption of chemical bleaching techniques were introduced. Therefore in addition to the production of mechanical pulp (Germany, 1844), the chemical soda pulp (England, 1851), sulfite pulp (United States, 1844), sulfate pulp (Germany, 1884) and semi-chemical pulp (United States, 1925) were manufactured.

The wood pulp contains residual lignin in spite of the delignification and bleaching treatments. The presence of that compound, extremely sensitive to photo-oxidation phenomena, even at low content, has the consequence of a premature yellowing of the paper.

Since the first half of the 19th century, papers contain a high percentage of lignin that causes a faster degradation of documents.

In addition to the fibrous raw materials, non-fibrous substances like glues, mineral fillers, dyes, bleaching agents and various additives, which are added to the mixture or applied on the surface of the paper, have a determining influence on the final quality of the product and they contribute to accelerate the deterioration of cellulose.

Glues are throughout used as surface paper sizing during the manufacturing processes. The Arabs practiced that procedure using vegetable glues based on starchy substances. In the XIV century, in Fabriano, the use of animal gelatin was introduced to prevent mold, in the XVII century the animal gelatin, which is also highly perishable, was stabilized by alum. In 1826 animal gelatin was replaced by colophony with alum until the recent replacement with synthetic resins. Besides waterproofing the fibers, alum and rosin protect the paper from microorganisms but also generate an acid reaction that accelerated degradation.

Mineral fillers, such as talc, kaolin, calcium carbonate and magnesium carbonate are added to paper pulp to reduce its porosity and thus making it smoother, less absorbent and more opaque. These substances exert a protection against acidification of the cellulose but produce a lower mechanical resistance of the paper.

Metal residues of cellulose making processes (iron, copper or aluminum) can also be found between the fibers thus contributing to the catalysis of oxidation phenomena.

Finally, organic or synthetic dyes have to be considered as concomitant causes of the degradation of paper. As an example, optical brighteners were introduced to enhance the impression of whiteness after the utilization of chlorine soda process.

The writing or printing of paper is a potential cause of degradation due to the nature of the inks.

The oldest ink, already used by the Egyptians[6], is composed by carbon black or bistro[7] suspended in water, oil and rubber. The carbon black was produced by depositing on a cold wall, in lack of air, the combustion products of resinous vegetable or charcoal. The resulting ink is resistant to light and the writing is stable over time. Anyway, problem of preservation arises from the aging of the dispersing medium, which tends to detach from the support.

Iron gall inks use dates back to the fourth century A.D. It has been used up to the beginning of the 20th century with particular applications during the Renaissance due to of their ease manufacture and permanence once applied on the paper. The invention of this ink belongs to China. from where in gradual steps from Arabia, Spain and France it finally reached Rome and from there wherever civilization existed[8]. The acidity of the iron inks is linked to the presence of tannic or sulfuric acid being. In fact the ink is an acidic aqueous suspension of ferrous sulfate, gall or tannic acid and Arabic gum. In some cases, it affects the paper fiber up to drill it.

Highly stable paper can be produced starting from an accurate selection of raw materials and environmental conditions. The paper should be manufactured from raw materials having high content of not oxidized cellulose and should contain alkaline fillers like calcium carbonate to prevent acidic degradation. Paper manufactured from cotton cellulose is more durable than paper manufactured by wood pulping. The pulping process, like conventionally bleached Kraft[9] or sulfite pulp, is aimed at removing as much lignin as possible without sacrificing fiber strength, thereby freeing the fibers from impurities that cause discoloration and possible future disintegration of the paper. In principle, cellulose fiber from any vegetable could be used for paper production, but the strength and quality of fiber varies among species. In particular, the softwoods yield long and strong fibers while hardwoods generally have shorter fibers and therefore produce a weaker paper but more opaque and better suited for printing. Both softwoods and hardwoods are used for

[6] Lucas, A. "The inks of ancient and modern Egypt." Analyst 47.550 (1922): 9-15.
[7] The bistro, brown ink, is made by a mixture of burnt beech wood powder.
[8] Carvalho, D. N. Forty Centuries of Ink Or, A Chronological Narrative Concerning Ink and Its Background, Etc. Bank Law Publishing Company, 1904.
[9] The kraft process is a process for conversion of wood into wood pulp and consists in treating wood chips with sodium hydroxide and sodium sulfide.

papermaking and are sometimes mixed to provide both strength and printability to the finished product[10].

Cellulose[11] is the main constituents of the paper and it is composed of anhydrous glucose units linked through a glycosidic bond (β-(1,4)-D-glucopyranose). It is a linear polymer whose chain length depends on the plant species that produced the cellulose. Cellulose from wood pulp has typical chain lengths between 300 and 1700 units; cotton and other plant fibers as well as bacterial cellulose have chain lengths ranging from 800 to 10,000 units[12]. The ability of –OH (hydroxyl) groups along the chain to link via hydrogen bond brings cellulose chains to be partially ordered. The hydrogen bonds, the uniform chemical constituents and the conformation of the chain make cellulose to possess relatively high molecular weight and promote ordered regions that have semi-crystalline properties.

In nature, most cellulose is produced as crystalline and is defined as cellulose I. It is composed of two distinct crystalline forms (triclinic cellulose Iα and monoclinic cellulose Iβ) that differ in their crystal packing, molecular conformation and intermolecular hydrogen bonding patterns[13]. These differences may influence the physical properties of the cellulose[14]. The ratio of the two phases depends on the origin of the cellulose. The Iα form is dominant in cellulose produced by primitive organisms, such as the bacterium Acetobacter Xylinum and the alga Valonia Macrophysa, whereas the Iβ form dominates in cellulose produced by higher plants. The Iβ form is more stable than the Iα form, which has been reported to be more susceptible to enzymatic hydrolysis[15]. Native cellulose contains also less ordered, amorphous or paracrystalline regions. So far, amorphous cellulose has not been widely studied. Kondo and Sawatari demonstrated that amorphous cellulose chain is bound by hydrogen bonds between the C2, C3 and C6 hydroxyl groups isotropically distributed[16].

[10] Andelin, J., Niblock, R. W.and Curlin J. W. "Technologies for reducing dioxin in the manufacture of bleached wood pulp." Background Paper (OTA-BP-O-54), US Congress, Office of technology assessment, Washington (DC), USA. 1989.
[11] Roberts, J. C., Bhalgat, M. K. and Zera R. T. "Preliminary biological evaluation of polyamidoamine (PAMAM) StarburstTM dendrimers." Journal of biomedical materials research 30.1 (1996): 53-65.
[12] Klemm, D., et al. "Cellulose: fascinating biopolymer and sustainable raw material." Angewandte Chemie International Edition 44.22 (2005): 3358-3393.
[13] Atalla, R. H., and Vanderhart D. L. "Native cellulose: a composite of two distinct crystalline forms." Science 223.4633 (1984): 283-285.
[14] Nishiyama, Y., et al. "Crystal structure and hydrogen bonding system in cellulose Iα from synchrotron X-ray and neutron fiber diffraction." Journal of the American Chemical Society 125.47 (2003): 14300-14306.
[15] Hayashi, N., et al. "The enzymatic susceptibility of celllose microfibrils of the algal-bacterial type and the cotton-ramie type." Carbohydrate Research 305.2 (1997): 261-269.
[16] Kondo, T., and Sawatari, C. "Intermolecular hydrogen bonding in cellulose/poly (ethylene oxide) blends: thermodynamic examination using 2, 3-di-O-and 6-O-methylcelluloses as cellulose model compounds." Polymer 35.20 (1994): 4423-4428.

Cellulose degradation occurs through various chemical, physical and biological factors and mechanisms that lead the paper to loss its mechanical properties[17]. Despite all, the fibers of the old papers are resistant to most of the chemical agents and the long molecular chains provide excellent mechanical strength.

Among the components of the wood pulp, the lignin is very unstable. Lignin is a complex of three-dimensional polymers that have in common a hydroxy- and a methoxy-substituted phenylpropane unit variously bonded. In nature it is very resistant to degradation, as a consequence of the strong chemical bonds holding together the various units and bonding them in complex and various ways to carbohydrates in wood. However the lignin compounds that occur in paper have been treated rather harshly and do not retain that structure. Lignin promotes acid degradation including embrittlement and discoloration. As a consequence, 19th, 20th and 21st century papers made by wood pulp has a high acid content and short cellulose chains.

The paper pulp contains also a non-negligible percentage of hemicelluloses and of substances chemically similar to cellulose. Hemicellulose is the common name for a large number of different carbohydrate heteropolymers, whose xylans and glucomannans are the main components. It is a heterogeneous mixture of different polysaccharides and its composition depends on the plant type. Apart from glucose, it may contain mannose, xylose, arabinose, rhamnose and L-fucose. Hemicelluloses are more reactive than the cellulose because of their non-crystallinity and of presence of reactive functional groups. J.C.Roberts[11] described their stability under acids and alkali condition. According to the author, the hemicelluloses are easily hydrolyzed by acid while their stability against alkali degradation is higher compared to that of the cellulose.

[17] Strlič, M., and Kolar, J., eds. Ageing and stabilisation of paper. Ljubljana: National and University Library, 2005.

## 1.2 Causes of Paper Degradation

In order to develop appropriate conservation and restoration of papers, it is important to understand the factors that cause degradation and their mechanisms of action in relation to the properties of paper. The main requirement of a proper conservation method is to remove the causes of degradation and to stabilize the paper by slowing the rate of the occurring processes.

Paper degradation is a complex phenomenon originating both from biotic and abiotic agents as sketched in figure 1.1.

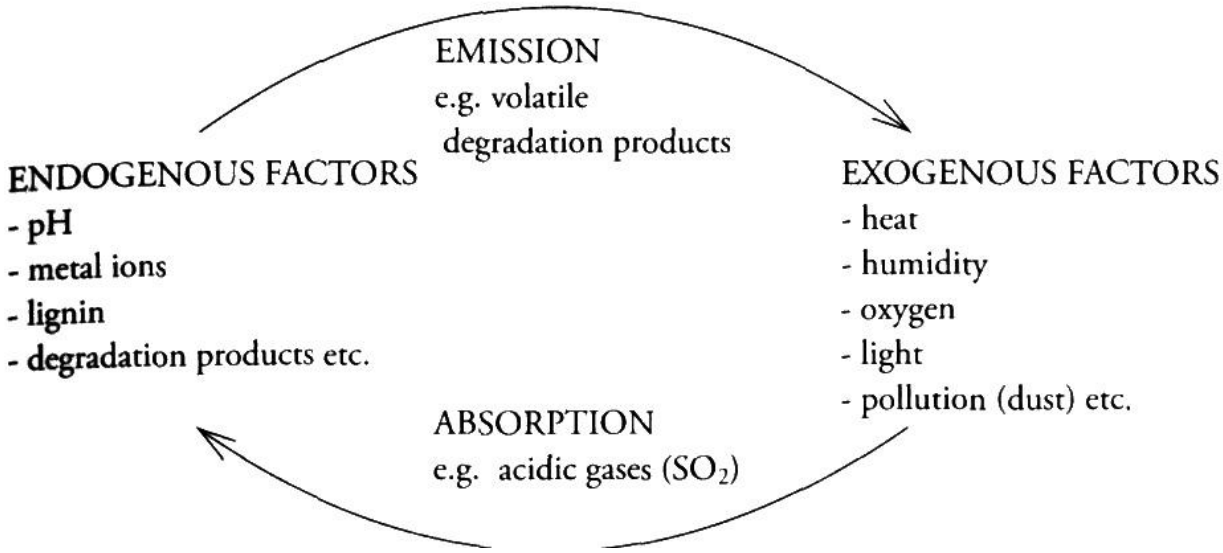


**Figure 1.1.** A simplified scheme of factors affecting paper stability[5].

***The chemical agents*** such as oxygen pollutants, metal ions, lignin, degraded products and others, cause the paper to undergo chemical degradation by directly reacting with or catalyzing the reactions of cellulose macromolecules. The occurring processes are hydrolysis, oxidation, chain breaking[7,18]. G. Artioli[4] discussed about the role played by metal ions in cellulose degradation. They act as catalyst or as Lewis donor-acceptor.

***The physical agents*** as humidity, temperature and illumination related to mechanical use and storage conditions can result in stress, loss of mechanical strength, yellowing, fading textural and

[18] Baty, J. W. et al. "Deacidification for the conservation and preservation of paper based work: A review." Review article. BioResources 5 (2010):1955-2023.

shape change of paper. Baty et al.[18] and Zervos[19] described the effect of temperature, relative humidity, pH, light and pollutant on the ageing process. These make the paper to loss its function and properties.

***The biological agents*** such as bacteria, fungi and protozoa can cause biological damage and their attack is promoted by the atmospheric humidity or by the water presence in paper already damaged[20]. Artioli[4] attributed the biological degradation to the action of microbial enzymes that chemically break down large molecules into smaller water-soluble units. To eradicate such attack and degradation, Baty et al.[18] and Area et al.[20] described excellent treatment options able to deacidify, strengthen and even protect from further deterioration.

All the above cases are classified by various authors into different categories depending on the sources of factors. For example Artioli[4] and Janssens[21] proposed two groups depending on the sources: internal and external.

***The internal causes*** are those related to paper composition, paper sizing and other components[12]. These include metals, adhesives, fillers, coating materials, salt, oxidizing compounds, impurities, pigments and inks.

***The external causes***[2] are those arising from environmental conditions, storage condition, use, disasters and wrong conservation treatment. The environmental conditions depend on storage environment. These includes temperature, relative humidity, light, ultraviolet radiation, dust, chemical and biological pollutants.

Pollutants[22,23] contributing to the acidity of paper include sulfur dioxide ($SO_2$), which can be oxidized to sulfur trioxide ($SO_3$) and then form sulfuric acid ($H_2SO_4$) in presence of moisture and nitrogen oxides ($NO_x$). The presence of trace metals autocatalyzes the oxidation processes including the oxidation of sulfur dioxide to sulfur trioxide. Ozone and various VOCs can oxidize cellulose and other paper components to acidic compounds.

[19] Zervos, S. "Natural and accelerated ageing of cellulose and paper: A literature review." Cellulose: Structure and properties, derivatives and industrial uses (2010): 155-203.
[20] Area, M. C. and Cheradame, H. “Paper ageing and degradation : Recent findings and research methods.” Peer – viewed review article. BioResources 6 (2011): 5307-5337.
[21] Janssens, K. and Van Grieken R., “Non-destructive micro analysis of cultural heritage materials”. Eds. Elsevier, 2004.
[22] Hudson, L. F. "Acidity of 17th and 18th century books in two libraries." Paper Technology 8.3 (1967): 189-190196.
[23] Baer, N. S., and Berman, S. M. "An evaluation of the statistical signicance of Hudson's acidity data for 17th. and 18th. century books in two libraries." Restaurator 7.3 (1986): 119-124.

## 1.3 Mechanisms of paper degradation

The variability in the chemical and physical degradation processes as well as their occurrence in solid state impedes their detailed understanding even if the main chemical and physical mechanisms in aqueous solution are well known. The two most important reactions responsible for the degradation of paper are hydrolysis and oxidation degradation.

***Hydrolytic degradation*** is an important reaction in which cellulose breakdown into its units during ageing. Hydrolysis causes the breaking of the *ß*-glycosidic bond inducing the depolymerization of cellulose. The process can occur both in acidic and alkaline environment and is called acid catalyzed hydrolysis and alkaline hydrolysis respectively. The acids perform their catalytic activities even at low temperatures while the alkaline substances have an appreciable effect at high temperatures.

***The acid-catalyzed hydrolysis*** is the most studied and understood degradation chemistry of cellulose. The acid hydrolysis reaction occurs in two steps via a nucleophilic substitution reaction. The reaction scheme is shown in figure 1.2.

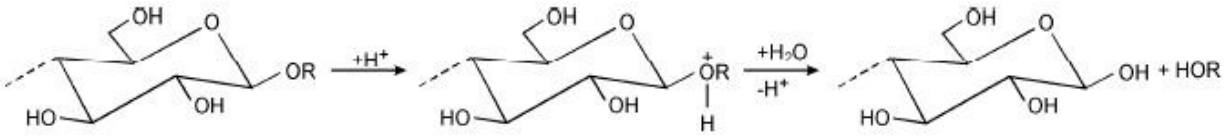


**Figure 1.2.** Acid-Catalyzed hydrolysis of cellulose[5].

A reactive intermediate is formed by the protonation of the oxygen atom in the glucosidic bond. The positively charged oxygen promotes the addition of a molecule of water to one of the two carbon atoms of the glycosidic bond, causing the cleavage of the bond. The protonated glucoside releases the proton thus re-establishing the initial acidity. According to this reaction mechanism, the rate of paper degradation will depend on the amount of water and on the concentration of $H^+$ ions, besides the rate of the hydrolytic process is determined also by the temperature[24,25].

[24] Williams, J. C. "A review of paper quality and paper chemistry." Library trends 30.2 (1981): 203-224.
[25] Zou, X., Uesaka, T. and Gurnagul, N. "Prediction of paper permanence by accelerated aging I. Kinetic analysis of the aging process." Cellulose 3.1 (1996): 243-267.

***The alkaline hydrolysis*** occurs trough a ß-alkoxyelimination reaction that results in chain cleavage[26]. Artioli[4] affirms that alkaline hydrolysis takes place only with strong alkalis at high temperatures. In high alkaline media[27], the reducing glucose end group of a cellulose molecule is subject to a number of isomerizations that result in migration of the carbonyl group along the carbon chain. The ketose or aldose end groups thus produced can undergo β-elimination. If β-elimination occurs at the level of C4 carbon atom, one hexose monomer unit is split off from the cellulose molecule and the next glucose end group can take part to the reactions. By means of this process the glucose units are released one by one from the cellulose molecule and the resulting is a depolymerization known as the peeling-off reaction. Once the β-elimination occurs at positions other than C4 the hexose unit remains attached to the cellulose molecule thus terminating the depolymerization. The cleavage mechanism is shown in figure 1.3.

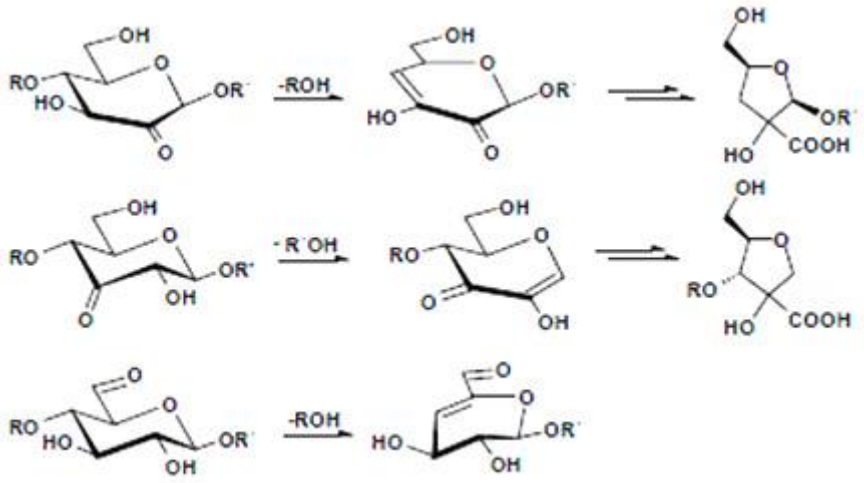


**Figure 1.3.** The cleavage of the glycosidic bond by ß-elimination starting at the oxidized structures along the cellulose

Corbett[28] affirms that alkaline hydrolysis can take place even at low alkali condition and room temperature when oxidized groups are present along the cellulose chain.

The formation of carbonyl group can occur in three ways: formation of aldehyde group from anhydroglucose unit (C6) which is further oxidized to carboxyl, formation of ketones by oxidation

[26] Pavasars, I., et al. "Alkaline degradation of cellulose: mechanisms and kinetics." Journal of Polymers and the Environment 11.2 (2003): 39-47.
[27] Kennedy, J. F., Cellulose and its Derivates: Chemistry, biochemistry and applications. Eds. Ellis Horwood, 1985.
[28] Corbett, W. M. "The alkaline degradation of chemically modified cellulose."Journal of the Society of Dyers and Colourists 76.5 (1960): 265-271.

of hydroxyl groups on C2 and C3 and possibility of production of an aldehyde end group by C2-C3 scission that can be transformed to carboxylic group[29].

Different authors have described alkaline hydrolysis of cellulose occurring after deacidification of paper. Ahn[29] reported the cellulose degradation after mass deacidification of library books. According to Ahn, the alkaline hydrolysis degradation by ß-elimination process did not produce significant effect after deacidification treatments of the naturally-aged library books. Malesic[30] showed the possibility of cellulose degradation after deacidification treatment. Mozdyniewicz [31] explained the possible way of slow down the ß-elimination reaction either chemically or physically. According to the author, the formation of stable acid at reducing end can prevent further degradation.

Alkaline degradation can be one of the most important reactions occurring when oxidized paper is deacidificated. For instance, Stephens[32] discussed about the resistance of oxidized papers against alkaline damage during deacidification treatment. He indicated that the reaction can take place at moderate alkaline pH. Thus it is crucial for studying rate of degradation of oxidized cellulose after treatment to know whether the degradation process is brought by deacidification treatment at appropriate pH value.

***Oxidation degradation,*** whose pathway is reported in figure 1.4, occurs when cellulose or paper components react with oxygen at ambient conditions.

The oxidation may be due to various causes and it generates various products. The degradation process involves three reaction steps: 1) free radical formation (chain initiation step) in the presence of light or radiation, 2) reaction of the so formed free radical to form another free radical and other products (chain propagation step), 3) chain termination in which free radicals recombine.

[29] Ahn, K. et al. "Is cellulose degradation due to β-elimination processes a threat in mass deacidification of library books?." Cellulose 19.4 (2012): 1149-1159.
[30] Malesic, J., Kolar J., and Strlič M. "Effect of pH and Carbonyls on the Degradation of Alkaline Paper Factors Affecting Ageing of Alkaline Paper."Restaurator 23.3 (2002): 145-153.
[31] Mozdyniewicz, D. J., and Sixta, H. "Carbohydrate degradation reactions during alkaline steeping of dissolving pulp-influence of air exclusion."Lenz. Berich 90 (2012): 103-107.
[32] Stephens, C. H., et al. "Hydrolysis of the amorphous cellulose in cotton-based paper." Biomacromolecules 9.4 (2008): 1093-1099.

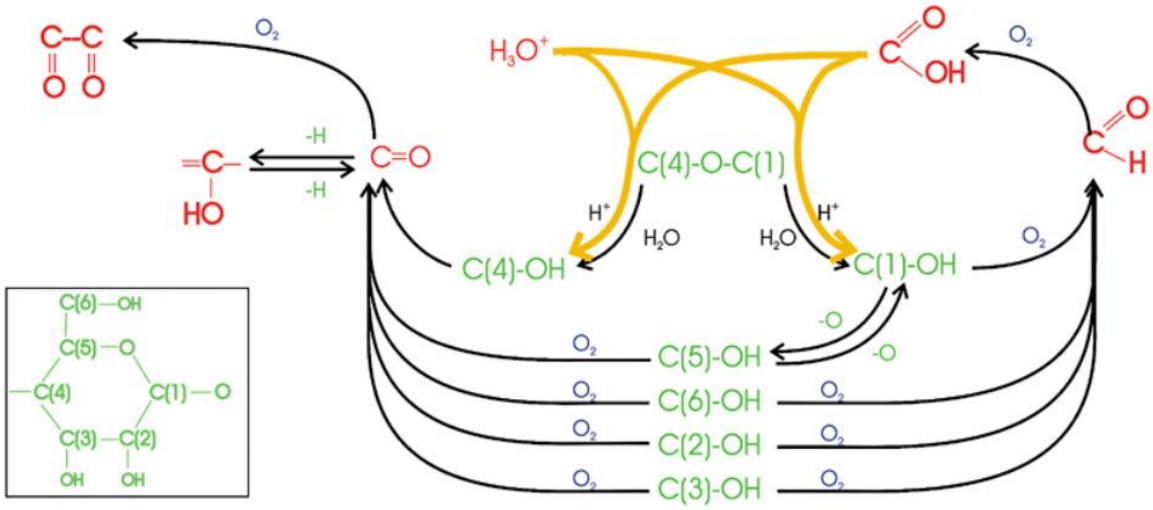


**Figure 1.4.** Pathways of oxidation of cellulose[129]

Oxidation of the paper results in change of physical properties, discoloration and increase of acidity[33]. Yellowing is due to the formation of conjugated double bonds (C=C) in cellulose chain or side chains. Similarly oxidation of cellulose breaks the cellulose (chain scission) to shorter chains resulting in reduction of molecular weight. The increment in acidity is due to the formation of carboxyl groups that in turn catalyze the hydrolysis reaction. The process is very complex due to the synergy between the reactions. Whitmore[34] explored a number of oxidizing treatments on filter papers, and a range of degradation paths have been observed, among them the carbonyl production is promoted by periodate, acidic hypochlorite, hydrogen peroxide and near ultraviolet light. The variety of oxidative degradation processes suggests that the probability of post-oxidative strength loss may depend on the nature of the original cellulose. This implies that the investigation of the above processes on laboratory specimens partially reproduces the mechanisms occurring in real case.

***Metal catalyzed oxidation*** of cellulose can occur on historical documents that contain metal ions deriving from iron gall ink and copper acetate pigments.[35] The oxidation occurs mainly on the

[33] Paulsson, M., and Parkås, J. "Review: Light-Induced Yellowing Of Lignocellulosic Pulps-Mechanisms And Preventive Methods." BioResources 7.4 (2012): 5995-6040.
[34] Whitmore, P. M., and Bogaard, J. "Determination of the cellulose scission route in the hydrolytic and oxidative degradation of paper." Restaurator 15.1 (1994): 26-45.
[35] Ahn, K., et al. "Investigation of the stabilization of verdigris-containing rag paper by wet chemical treatments." Heritage Science 2.1 (2014): 12.

widespread foxing and on the progressive bleeding of the writing area. In particular Neevel[36] has detected a correlation between the excess ferrous sulfate in the ink and the paper degradation.

Some authors [37] consider that metal acts as a catalyst in the homolytic scission of the cellulose peroxide with a radical mechanism. Other authors[38] postulate a donor-acceptor Lewis mechanism involving either the semiacetalic oxygen on the anhydroglucose unit or the β-glucosidic oxygen.

Artioli[2] described the catalytic and donor–acceptor role played by iron ion in the homolytic scission of the cellulose peroxide and cleavage of a glucopyranose bond as well as depolymerization of cellulose chain. He described that the iron(II) ion can speed up oxidative degradation of cellulose in two ways: either by promoting the formation of organic radicals then followed by oxidation of cellulose or formation of reactive hydroxyl radicals interacting with cellulose to form organic radicals.

The harmful effects of iron gall inks on the carrier were scientifically confirmed. When used on paper, this ink induce high damages, due to the presence of organic acid that leads to very acidic pH values and consequentially to cellulose acid hydrolysis, and to the presence of iron(II) that catalyzes cellulose oxidation. J. Kolar et al.[39] studied historical documents containing iron gall inks and quantified its effect on the paper stability. V.S. Sˇelih et al.[40] experimented the effect of transition metals in oxidative degradation of cellulose and their roles during oxidative degradation of paper.

[36] Neevel, J. G. "Phytate: a potential conservation agent for the treatment of ink corrosion caused by irongall inks." Restaurator 16.3 (1995): 143-160.
[37] Shahani, C.J., Hengemihle, F.H. The influence of copper and iron on the permanence of paper, in Historic textile and paper materials, conservation and characterization (Advances in Chemistry Series, n. 212), ed. by H. Needles and S. H. Zeronian, Washington D.C. 1986, p. 387- 410
[38] Sarybaeva, R. I., et al. "Degradation of cellulose in the presence of Lewis acids." Cellulose chemistry and technology 25.3-4 (1991): 199-210.
[39] Kolar, J. et al. "Stabilisation of corrosive iron gall inks." Acta Chimica Slovenica 50.4 (2003): 763-770.
[40] Šelih, V. S., et al. "The role of transition metals in oxidative degradation of cellulose." Polymer degradation and stability 92.8 (2007): 1476-1481.

## 1.4 The polymerization degree.

The polymerization degree is an important parameter for the study of the degradation of the paper. The polymerization degree can undergo a reduction in its value, because of the treatments carried out in the production of the paper and because of the presence of particular substances. The depolymerization reduces a long chain in shorter chains causing an increase in the fragility of the paper.

DP is the degree of polymerization at time t of degradation process, and is equal to DP = M1/(M0+S). M1 is the total number of repeats units ∑nPn, i. e. it is the first order moment of molecular weight distribution, M0 is the total number of polymer molecules $\Sigma$Pn, or zero order moment of the molecular weight distribution, S is the number of scissions, Pn is defined as the number of polymer molecules of degree of polymerization n, M1 gives the sample weight when multiplied by the molecular weight of the repeat unit.

The polymerization degree variation rate, equal to the number of broken bonds per anhydroglucose unit, was described by the linear Ekenstam approximation[41]:

$$1/DP - 1/DP^{\circ} = kt \qquad (1)$$

where the symbols are as above and $DP^{o}$ is the value at time zero, and is equal to M1/M0.

Some theorists[42] developed a first-order kinetic equation that link the number of broken bonds expressed in terms of mmol of scissions S in 100 g of cellulose, to the polymerization degree:

$$S = n^{\circ}(1/DP - 1/DP^{\circ}) \qquad (2)$$

Where n° is the initial number of scissile glycosidic linkages.

[41] Ekamstam, A. "The behaviour of cellulose in mineral acid solutions: kinetic study of the decomposition of cellulose in acid solution." Ber. Deutschen Chem. Gesellschaft 69 (1936): 553.
[42] Montroll, E. "Molecular size distributions and depolymerization reactions in polydisperse systems." Journal of the American Chemical Society 63.5 (1941): 1215-1220.

Ekenstam derived the above kinetic model by assuming that the reaction is a first order one. The Ekenstam model was fruitfully utilized[43] when the evaluation of the activation energy of the hydrolytic degradation of cellulose and its synthetic derivatives was the main goal of cellulose scientists. In fact, the different values of k obtained in different laboratories with different samples and different values of n° yielded different intercepts (frequency factors) but the same slope (activation energy) of the Arrhenius equation[44]. This Ekenstam kinetic equation has been successfully applied to cellulose degradation in liquid acidic and alkaline media and also to thermal degradation at high temperatures (120-200°C). Recently, it has been tested for cellulose degradation in the accelerated aging of paper[45].

Zou et al[46] modeled the degradation process without any assumption about the reaction order, and show that the model that brings to the equation (1) is a special case of a more general model, which is obtained if the rate of bond scission is assumed to be constant throughout the reaction.

Emsley[47] reported an empirical model that relates change in degree of polymerization and change in tensile strength during ageing cellulose paper and the degradation data is better represented by a model which allows the rate of scission to decrease exponentially as the reaction proceeds giving more accurate predictions of the time to attain low DP values.

[43] Calvini, P. "The role of the Ekenstam equation on the kinetics of cellulose hydrolytic degradation." Cellulose 19.2 (2012): 313-318.
[44] Emsley, A. M., and Stevens G. C.. "Kinetics and mechanisms of the low-temperature degradation of cellulose." Cellulose 1.1 (1994): 26-56.
[45] Zou, X., Uesaka, T. and Gurnagul, N. “Prediction of paper permanence by accelerated ageing: Part 1 Kinetic analysis of the aging process”. Cellulose 3 (1996), 243–267.
[46] Zou, X., Gurnagul, N., Uesaka, T. and Bouchard, J. “Accelerated ageing of papers of pure cellulose: Mechanism of cellulose degradation and paper embrittlement”. Polym. Degrad. Stab. 43 (1994), 393–402.
[47] Emsley, A. M., et al. "Degradation of cellulosic insulation in power transformers. Part 2: Formation of furan products in insulating oil." IEE Proceedings-Science, Measurement and Technology 147.3 (2000): 110-114.

## 1.5 Crosslinking reactions.

Crosslinking is a chemical process in which two or more molecules belonging to different cellulose chains are joined through a covalent or ionic bond. The name aldo refers to the event that brings the chains linked together to lose some of their ability to move as individual chains. Crosslinks can be induced chemically under different conditions like heat, pressure, pH or radiation.

During the thermal ageing of cellulose, crosslinking results in the increase of the wet-strength[48] and in the decrease of the wet elongation[49]. The wet strength increase is assumed to depend on intra-fiber and inter-fiber crosslinking. High-molecular weight molecules favor the formation of inter-fiber crosslinking, which improves the dry strength and the durability of the material. Low-molecular weight molecules gives intra-fiber crosslinking that causes embrittlement of fibers and decreases the flexibility of the material[50].

Crosslinking is speculated to occur also during natural ageing[51]. Page[52] had shown that the strength of paper could depend on the strength of the fibers as well as on the strength of the bonds connecting them. During thermal treatment the fiber bonding strength increases whereas the fiber strength decreases in agreement with the wet strength increases[53]. Probably the crosslinking reactions contribute to increase the rigidity of paper during natural and accelerated ageing, although it has not yet been possible to separate the physical and chemical influences on the elasticity[54].

The crosslinking reactions are acid catalyzed as demonstrated by the wet strength increases at low pH or in the presence of Lewis acids. Aldehyde or ketone groups on carbon atom 2 or 3 can react with hydroxyl groups in a crosslinking reaction thus form hemiacetal or hemiketal bonds among cellulose chains. Probably carbonyl-containing degradation products can crosslink the cellulose chains during acetal- and ketal-forming reactions. Carboxyl groups (e.g. from uronic acid groups in hemicellulose) and the hydroxyl groups of the cellulose can also react to form ethers[55].

[48] The wet strength of paper is a measure of how the web of fibers can resist a force of rupture when the paper is wet.
[49] Wet elongation is the tensile strain developed in the wet paper at maximum tensile strength before rupture.
[50] Xu, G. G., and Yang, C. Q.-X. (1999). "Comparison of the kraft paper crosslinked by polymeric carboxylic acids of large and small molecular sizes: Dry and wet performance." Journal of Applied Polymer Science, 74, 907–912
[51] Graminski, E. L. "The stress-strain behavior of accelerated and naturally aged papers." Tappi J. 1970, 53, 406-410.
[52] Page, D. H. "A theory for tensile strength of paper." *Tappi* 52.4 (1969): 674.
[53] Espy, H. H. "The mechanism of wet-strength development in paper: a review." Tappi Journal 78.4 (1995): 90-100.
[54] Zou, X., et al. "Accelerated aging of papers of pure cellulose: mechanism of cellulose degradation and paper embrittlement." *Polymer degradation and stability* 43.3 (1994): 393-402.
[55] Wilson, W. K., and Parks, E. J. "An analysis of the aging of paper: Possible reactions and their effects on measurable properties." *Restaurator* 3.1-2 (1979): 37-62.

The above acid catalyzed reactions coupled with a high drying temperature lead to the formation of irreversible or partially reversible hydrogen bonding in paper upon water removal. This phenomenon is called hornification[56].

[56] Diniz, JMB F., M. H. Gil, and J. A. A. M. Castro. "Hornification—its origin and interpretation in wood pulps." Wood Science and Technology 37.6 (2004): 489-494.

## 1.6 Natural and accelerated ageing of cellulose and paper

Accelerated ageing constitutes the major methodological tool for studying cellulose and paper degradation. The study of the natural ageing of cellulose can take several years to affect on certain cellulose properties, and even several decades to produce statistically significant changes. The best method to study ageing of paper is to expose it to hostile environments that are more aggressive than the normal environment.

Accelerated aging at high temperatures unfortunately is not able to produce the same effects of natural degradation. In fact high temperature accelerates different reactions or disturbs the equilibrium among them producing spurious results[57]. Bansa questioned the credibility of the accelerated ageing tests[58] concluding that there is no correlation between natural and accelerated ageing. Otherwise, the use of accelerated ageing is accepted for determining if a process (i.e. an innovation in the production or a paper conservation intervention) can speed or slow the ageing rate of a specific paper. In another study, Zou compared predictions based on the Arrhenius equation to the results of natural ageing for 22 years on lignin-free paper, and found a good correlation between natural and accelerated ageing. Zou concluded that *"the accelerated ageing test using the empirical Arrhenius procedure has a potential to predict natural ageing behavior if factors affecting the frequency factors of each reaction, such as moisture content, hydrogen ion concentration, oxygen content, etc. are kept the same between natural ageing and accelerated ageing".*

Shahani[59] compared the natural with the accelerated ageing. He found that both processes produced the same products at about the same proportions. In addition Shahani developed the ASTM/ISR Research Program on the Effects of Aging on Printing and Writing Papers in which the 15 libraries involved will give samples every 10 years for the next 100 years. The results will be used to improve the correlation between accelerated and natural ageing.

The first standard concerning the accelerated ageing of paper was established with TAPPI T 453 (and later regulated by ISO 5630-1). This standard specifies the use of dry heat treatment (105 °C) in order to accelerate the ageing of paper. The recognition of the effects of moisture and the need to simulate the naturally occurring ageing had led to the introduction of moist ageing. Many methods

[57] Bansa, H. "Accelerated ageing of paper: Some ideas on its practical benefit." *Restaurator* 23.2 (2002): 106-117.
[58] Bansa, H. "Accelerated aging tests in conservation research: some ideas for a future method." *Restaurator* 13.3 (1992): 114-137.
[59] Shahani, C., Lee, S. B., Hengemihle, F. H., Harrison, G., Song, P., Sierra, M. L., Ryan, C. C., Weberg, N. Report on: Accelerated aging of paper: I. Chemical analysis of degradation products. II. Application of Arrhenius relationship. III. Proposal for a new accelerated aging test: ASTM research program into the effect of aging on printing and writing papers; Library of Congress: 2001.

of moist ageing have been proposed, the most used is a treatment at 80 ºC and 65 %RH as regulated by TAPPI T 402 and ISO 5630-3. The relationship between this artificial aging method and natural aging at 23 °C and 50 %RH is reported in literature [60]. In particular it was established that, for Whatman no. 1 paper, 7 days of artificial aging correspond to 10 years of natural aging conditions.

Although artificial ageing cannot predict quantitatively the life expectancy of paper and it is impossible to strictly correlate artificial ageing with natural ageing times, it can still predict *"where our paper are going"*[61]. Calvini pointed out that by using accelerated ageing test it is possible to develop method for evaluation of the kinetic path of paper degradation and for evaluation of conservation treatments[62,19].

[60] Bicchieri, M., Bortolani, M., Veca, E.. Characterization of low-molecular-weight polyvinyl alcohol for restoration purposes. *Restaurator*, *14*.1 (1993), 11-29.
[61] Calvini, P. and Gorassini, A.. "On the rate of paper degradation: lessons from the past." *Restaurator* 27.4 (2006): 275-290.
[62] Inaba, M. et al. "The effect of cooking agents on the permanence of washi (Part II)." Restaurator 23.3 (2002): 133-144.

# *CHAPTER II*

# *METHODOLOGIES IN PAPER CONSERVATION EVALUATION*

## 2.1 Preservation Methodologies

The studies of deterioration and conservation of paper are being growing and require the setting up of methods and treatments that can stabilize and strengthen the paper. Various conservation treatments using different chemicals and various methods are being applied to model and real paper and their efficiency is being under investigation.

Zervos[19] published in 2006 a review in which the criteria for the characterization of the efficiency of a paper conservation intervention are listed. A successful intervention brings immediate improvement of paper properties like strength and pH and slows the paper ageing as evaluated through studies of degree of polymerization, pH and oxidation under artificial ageing. In addition, a proper intervention induces improvements of aesthetic and legibility. The efficiency of the conservation interventions is usually evaluated on standard paper such as Whatman filter paper and later on original historical paper. Durability of results is studied by means of accelerated aging as the one described in ISO 5630-3 (80 °C and 65 %RH). The physicochemical properties are determined before, during and after ageing of treated and untreated paper.

Deacidification treatment methods have been developed for stabilizing and preventing paper degradation due to acidity. These are applied to paper in order to neutralize the acid and form deposit of alkaline reserve. Baty[18] provided a review for different deacidification compounds that have been used. The compounds used for deacidification are often weak bases like carbonates, bicarbonates, some hydroxides, various oxides and amines. Alkaline earth carbonates like calcium carbonate and magnesium carbonate are widely used for deacidification due to their low cost, high brightness and suitability for use as paper fillers. Santucci[63] reported cases in which magnesium compounds in opposition to calcium ones caused accelerated aging of pure cellulose paper. Among them, calcium carbonate tends to buffer the pH in a moderate alkaline range. In addiction bicarbonates of calcium and magnesium are used due to their higher solubility in water and various studies[64] report their beneficial effects on the stability of paper strength and brightness. Italian

[63] Santucci, L. "Degradation of cellulose in the presence of inorganic compounds." Bollettino ICPL 1973, 32, 73-78.
[64] Lienardy, A. "A bibliographic survey of mass deacidification methods", Restaurator, 12 (1991): 75-103.

restorers widely use calcium propionate, as prescribed by "Istituto Centrale per la Patologia del Libro" (ICPL)[65].

Calcium hydroxide is one of the most used deacidification agent by restorers[66]. In particular saturated aqueous solution of $Ca(OH)_2$ diluted 1:1 with deionized water to prevent $CaCO_3$ precipitation before the hydroxide has penetrated into the fiber with the undesired effect of a surface deposition of the insoluble carbonate. Due to the low solubility of alkaline earth hydroxides in aqueous and non-aqueous media, recent investigations have focused on hydroxides nanoparticles. Some researchers showed that nanolime particles dispersed in aqueous and alcoholic media can be applicable for paper conservation and showed good results. Sequeira[1] evaluated the efficiency of paper deacidification with $Ca(OH)_2$ nanoparticle dispersed in aqueous and non-aqueous media including their use of items inscribed with iron gall ink. Likewise, Poggi et al.[2] experimented the applicability of alkaline earth hydroxide ($Ca(OH)_2$ and $Mg(OH)_2$) nanoparticles dispersed in alcohol for preventing ink-induced degradation of paper. Moreover the authors explained that the deacidification using nanosuspensions provide excellent penetration in the paper with homogenous distribution and ensure long term preservation. Stefanis and Panayioutou[67] deacidified paper with micro and nanoparticles dispersion of calcium and magnesium hydroxides and reported evidence of cellulose breakdown when pristine paper was treated. These adverse effects were attributed to the excessively high pH.

For the degradation induced by iron gall ink, both deacidification and reduction treatments should be required for conservation. Strlič[17] proposed the use of tetrabutylammonium bromide and other alkylimidazolium bromides for limiting the oxidative degradation. The antioxidant action of these compounds can deactivate or inhibit the oxidation by interfering with the reaction pathway and by forming complexes with metal ions.

An interesting option for paper conservation is the simultaneous use of deacidification and reduction treatment. Researches used various antioxidants agents to inhibit oxidation of cellulose and to bleach paper. In the past, for conservative purposes a number of oxidizing bleaches have been considered, like hypochlorite and hydrogen peroxide. Unfortunately these cause damage on

[65] Capitolato speciale tecnico ICPAL 2005
http://www.icpal.beniculturali.it/allegati/Capitolato_Speciale_Tecnico_Tipo.pdf
[66] Williams, J. C. "Chemistry of the Deacidification of Paper. *Bulletin of the American Group. International Institute for Conservation of Historic and Artistic Works*," *12*.1 (1971): 16-32.
[67] Stefanis, E. and Panayioutou, C., "Protection of lignocellulosic and cellulosic paper by deacidification with dispersions of micro- and nano-particles of $Ca(OH)_2$ and $Mg(OH)_2$ in alcohols" Restaurator, 28.3 (2007): 185-200.

cellulose fibers[68]. It has been demonstrated that reducing bleaches have fewer negative effects on cellulose. Conservators nowadays use three reducing bleaches: sodium dithionite, borohydride salts and alkylamine-boranes. Researchers from different areas showed the effectiveness of tert-butylamine borane complex (TBAB) for paper conservation. Researchers from "The Istituto Centrale per la Patologia del Libro (ICPL) of Rome" experimented and showed the usage of TBAB as reducing agent for the carbonyl functions groups. For instance Bicchieri[69,70,71,72] experimented TBAB on cellulose materials and found that the TBAB treatment method yield excellent outcomes. Later, the same research group studied the effectiveness and application of TBAB and showed that its effectiveness ranges from 50 to 80 % in the reduction of oxidized function and it is applicable even on printed papers. From the comparison of the effectiveness of different borane complexes it emerges that TBAB is one of the three best compounds and can be used in organic solutions. Moreover, Bicchieri conducted an experiment by applying simultaneous deacidification and reduction in non-aqueous medium using TBAB and calcium propionate on model paper and found that the paper stability is improved with respect to the deacidification treatment alone.

[68] Burgess, H. D. "Practical considerations for conservation bleaching."*Journal of the International Institute for Conservation-Canadian Group (J. IIC-CG)* 13 (1988): 11-26.
[69] Bicchieri, M. Bella, M. and Semetilli, F.M.. "A quantitative measure of borane tert-butylamine borane complex effectiveness in carbonyl reduction of aged papers." Restaurator 20.1 (1999): 22-29.
[70] Bicchieri, M. Sementilli, F.M. and Sodo, A. "Application of seven borane complexes in paper conservation." Restaurator 21.4 (2000): 213-228.
[71] Sanna, C. et al. "tert-butylamine borane complex: An unusual application of a reducing agent on model molecules of cellulose based materials." Journal of Cultural Heritage 10.3 (2009): 356-361.
[72] Bicchieri, M. et al. "The Indian drawings of the poet Cesare Pascarella: non-destructive analyses and conservation treatments." Analytical and bioanalytical chemistry 402.4 (2012): 1517-1528.

## 2.2 Characterization Methodologies

The methodologies mostly used for paper characterization are those applied for the paper industry process control. With very few exceptions no methods have been developed specifically for the evaluation of the efficiency of conservation treatments. Paper conservation is a relatively new scientific field involving a limited number of scientists and conservators traditionally highly skilled but empirically educated. Moreover, the paper conservation is practiced by individuals or public organizations with limited resources. In contrast, the paper industry has a long history in quality control processes. Besides paper industry is subject to market laws and competition, with huge investment for improving quality of paper.

The use of scientific techniques in book conservation has remarkably expanded in recent decades. There is much attention in identifying the materials used in cultural artifacts. A clear understanding of the state and mechanisms of degradation of objects susceptible of deterioration with time and exposure to environmental factors is of great importance. The knowledge of the state of materials at a molecular level can provide valuable information for conservators, enabling them to decide on a conservation procedure. Once a material is applied for conservation, it has to be underlined that an accelerated aging test does not tell what a paper will be like after 25 or 50 years of storage but only provides information concerning the ranking of different samples with respect to storage conditions.

It is important to determine which properties of paper should be included in an evaluation study and which protocol of analysis would be the most suitable for their measurement. The chosen properties should be measured by methods sensitive to the changes induced by the conservation treatment. Economy of time and resources determines the number of tests that should be kept to a minimum.

Many analytical techniques used in laboratories could provide information regarding the elemental composition, molecular structure and physical properties. Once an analytical technique suitable for studying a valuable artifact is chosen, it will be necessary to minimize the damage to the object, so non-invasive methods are preferred. When the required information can be accessed only by invasive techniques, their application should require quantity of material as small as possible.

Mostly of the applied techniques are those that give information on the mechanical properties as well as on some chemical parameters. As an example, Wilson and Parks[56] recommended the following tests for detecting changes during the ageing of paper: folding endurance, tearing strength, elongation, tensile energy absorption, zero span tensile strength (fiber strength), wet tensile (crosslinking), pH, alkali solubility (some chain scission and alkali sensitivity), functional

group content (oxidation), molecular chain length distribution (chain scission), copper number, viscosity. They affirmed that the above tests tell "what happens" during the ageing of paper but are not particularly useful for identifying the nature of the change. In recent years the improvements in instrumentation and methodologies had allowed the study of molecular parameters able to deepen the knowledge about the nature of changes occurring in conservation procedures. In principle, every technique able to detect a physical or a chemical parameter can be applied to investigate the state of paper. In what follows a short survey concerning the methods chosen in this thesis for the evaluation of paper properties and conservation treatments is reported.

*Surface pH measurement of paper* is a non-destructive test that is used to measure the hydrogen ion concentration (pH) on the surface. This method is used as an alternative to TAPPI T 509 "Hydrogen Ion Concentration (pH) of Paper Extracts-Cold Extraction Method," and TAPPI T 435 "Hydrogen Ion Concentration (pH) of Paper Extracts-Hot Extraction Method" because it avoids the destruction of printed material. pH values obtained through the application of this method to sized materials such as writing, printing and industrial papers reflect only the pH of the surface and should not be compared with bulk pH values determined by the water extraction methods.

*Colorimetry*[73] measures an absolute physical quantity defining the colors avoiding the subjective answer of the observer. Color can be measured according to the standards TAPPI T 524 and TAPPI 527. In order to point out possible phenomena of chromatic alteration and in order to understand to which extent the current condition of conservation are at the basis of alterations/degradations processes, different measurements have to be carried out on the same surface at various times. The contribution of colour measurements to the evaluation of paper conservation interventions is invaluable, since they make possible the objective aesthetic evaluation. The main problem of the colorimetric survey is linked to the repeatability of the measurement, i.e. the possibility to reproduce the same measurement conditions in time. To this purpose, the L*, a* and b* coordinates of the three-dimensional CIEL*a*b* (1976) color space have been introduced[74] and gradually started to replace the "traditionally" used optical parameter "brightness" in paper conservation evaluation.

*Nuclear Magnetic Resonance spectroscopy* is a powerful investigation tool useful to get information at a molecular level. Improvement on the instrumentation had allowed investigating samples both in

[73] Lorusso, S. Natali, A. and Matteucci, C. "Colorimetry applied to the field of cultural heritage: examples of study cases." Conservation Science in Cultural Heritage 7 (2007): 187-220.
[74] Carme, S., Gibert, M., and Areal, R. "Ageing of laboratory irongall inks studied by reflectance spectrometry." Restaurator 20.3-4 (1999): 151-166.

solid and in liquid state. Recent techniques as Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance ($^{13}C$ {$^{1}H$} CP MAS NMR) allowed to study the structure of materials and to perform studies about the interactions among components and thus the dynamic of systems. Once applied on paper $^{13}C$ {$^{1}H$} CP MAS NMR allowed obtaining information on the state of conservation and knowing the extent of oxidative and hydrolysis degradation directly in solid state[75]. Besides, $^{1}H$ NMR relaxations experiments on water in confined environment allowed obtaining information about pore size[76].

*Fourier Transform–Infrared spectroscopy* can supply data on the chemical changes occurring during ageing. IR spectra are characteristic of the chemical bonds present in sample and can provide a 'fingerprint' to identify different chemical functional groups. In particular Attenuated Total Reflectance-FT-IR spectroscopy[77] is a non-invasive technique that gives insight about the functional group of molecules at the sample surface. Hon[78] showed the FT-IR efficiency for studying acid substances in ancient and modern Chinese papers belonged to XVIII and XIX centuries. Zotti[79] analyzed the main surface components of eighteenth century papers by identifying gelatin, cellulose, calcium carbonate, gypsum, hemicelluloses and glue. Infrared spectroscopy can be used, with reserve, for estimating the amount of oxidized groups in cellulose[80]. In fact, it has to be taken into account the IR absorbance dependence on moisture content and the ability of aldehyde groups to bond water or alcohol to form hydrates or hemiacetals. Besides, conjugated oxidized groups give signals in the region of the spectrum where adsorbed water covers all signals with a strong band.

*Raman spectroscopy* can be applied to detect the presence of additives in the cellulose. As an example, Raman analysis of a seventeenth century map showed the gypsum use as an additive in the cellulose[81]. Bicchieri[82] have examined the cellulose subjected to wet accelerated aging which

[75] Proietti, N., Capitani, D., Pedemonte, E., Blümich, B., Segre, A. L., "Monitoring degradation in paper: non-invasive analysis by unilateral NMR. Part II", *Journal of Magnetic Resonance*, 170.1(2004), 113-120.
[76] Paci, M., Federici, C., Capitani, D., Perenze, N., Segre, A. L., "NMR study of paper, *Carbohydrate Polymers"*, 26.4 (1995), 289-297.
[77] Manso, M., and Carvalho M.L.. "Application of spectroscopic techniques for the study of paper documents: A survey."Spectrochimica Acta Part B: Atomic Spectroscopy 64.6 (2009): 482-490.
[78] Hon D., "*Fourier-Transform IR Spectroscopy and Electron-Spectroscopy for Chemical Analysis — Use in the Study of Paper Documents"*, Advances in Chemistry Series, 212 (1986), 349 - 361.
[79] Zotti M., Ferroni A., Calvini P., "*Microfungal Biodeterioration of Historic Paper: Preliminary FTIR and Microbiological Analyses"*, International Biodeterioration & Biodegradation, 62 (2008), 186 - 194.
[80] Calvini, P., Conio, G., Lorenzoni, M., & Pedemonte, E. "Viscometric determination of dialdehyde content in periodate oxycellulose. Part I. Methodology". *Cellulose*, *11*.1 (2004), 99-107.
[81] Castro K., Pessanha S., Proietti N., Princi E., Capitani D., Carvalho M.L., Madariaga J.M., "*Noninvasive and Nondestructive NMR, Raman and XRF Analysis of a Blaeu Coloured Map from the Seventeenth Century*, Analytical and Bioanalytical Chemistry", 391 (2008):. 433 - 441.

gives rise to a characteristic pattern of carbonyl groups. Moreover, Lojewska observed their vibrational modes [83].

T*he amount of carbonyl groups content* could be measured spectrophotometrically according to the procedure[84] based on the conversion of 2,3,5-triphenyltetrazolium chloride (TTC) by carbonyl into typhenylformazane, a red dye. The selectivity of the TTC reaction on reducing carbonyl groups was confirmed by Strlic[13] for a number of model compounds.

*The polymerization degree* allows the study of the deterioration process during ageing. The polymerization degree could be measured thought the evaluation of viscosity of pulp via the TAPPI method T230 "Viscosity of pulp (capillarity viscometer method)". The solution viscosity of the pulp gives an indication of the average degree of polymerization of the cellulose and a relative indication of the degradation (decrease in cellulose molecular weight) resulting from the pulping and/or bleaching process. The polymerization degree can be determined by Size Exclusion chromatography (SEC)[55] by registering the molecular weight distributions of cellulose tricarbanilate. The method for cellulose tricarbanilate preparation is to react the cellulose with phenyl isocyanate using pyridine as both solvent and catalyst.

*The folding endurance* is the most popular among the mechanical properties. Folding endurance measures the durability of paper when repeatedly folded under constant load and determines how many times the paper can be folded until it breaks. The folding endurance test measures a combination of tensile strength, stretch, and fatigue properties. This test is useful for measuring the deterioration of paper upon aging as it is sensitive to changes that show up prior a change in tensile, burst, or tearing resistance is manifested. The folding strength is quoted as the number of double folds. The folding endurance is the log10 of the number of double folds that a paper strip, held under tension, could endure before it breaks. Various instruments can be used for the measurement. The folding endurance can be measured by following the TAPPI T511 method or the ASTM D 2176 method by using various instrumentation: Kohler Molin, Lhomargy, MIT and Schopper[85].

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[82] Bicchieri M., Sodo A., Piantanida G., Coluzza C., "*Analysis of Degraded Papers by non-Destructive Spectroscopic Techniques"*, Journal of Raman Spectroscopy, 37 (2006):pp. 1186 - 1192.
[83] Łojewska, J., et al. "Carbonyl groups development on degraded cellulose. Correlation between spectroscopic and chemical results." Applied Physics A 89.4 (2007): 883-887.
[84] Szabolcs, O. V. "Eine kolorimetrische Methode zur Bestimmung der reduzierenden Carbonylgruppen in der Cellulose." Das Papier 15.2 (1961): 41-44.
[85] ISO 5626 (1993): Paper – Determination of folding endurance

## *SECOND PART*

## *CHAPTER III*

# *DEACIDIFICATION OF PAPER: NEW SYNTHESIS METHODOLOGY OF CALCIUM HYDROXIDE NANOPARTICLES AND EVALUATION OF THEIR EFFICIENCY*

## 3.1 Introduction

In the last years, the use of $Ca(OH)_2$ nanoparticles in the field of cultural heritage has been extensively applied for its significant role proposed in the conservation treatments[86,87,88]. Many works have been published about the application of $Ca(OH)_2$ nanoparticles to restoration of frescoes[89,90], wall paintings [91,92], stones[93,94] as well as to the deacidification of paper and canvas[95,96].

Nanolime is an excellent deacidifying agent for cellulosic materials. It ensures a good physicochemical compatibility with the support, and after its transformation into calcium carbonate,

[86] Baglioni, P., Chelazzi D., Giorgi, R. Nanotechnologies in the Conservation of Cultural Heritage: A compendium of materials and techniques. Springer, 2014. ISBN: 978-94-017-9302-5

[87] Baglioni, P., Chelazzi D., Giorgi R., Poggi G., Colloid and Materials Science for the Conservation of Cultural Heritage: Cleaning, Consolidation, and Deacidification. Langmuir, 29.17 (2013), 5110-5122.

[88] Giorgi, R., Baglioni M., Berti D., Baglioni P., New Methodologies for the Conservation of Cultural Heritage: Micellar Solutions, Microemulsions, and Hydroxide Nanoparticles, Accounts of Chemical Research, 43.6 (2010), 695-704.

[89] Natali, I., Saladino, M. L., Andriulo, F., Martino, D. C., Caponetti, E., Carretti, E., Dei, L. Consolidation and protection by nanolime: Recent advances for the conservation of the graffiti, Carceri dello Steri Palermo and of the 18th century lunettes, SS. Giuda e Simone Cloister, Corniola (Empoli). *Journal of Cultural Heritage*, 15.2 (2014), 151-158.

[90] Felice, B., Taglieri, G., Rigaglia, D., Arrizza, L., Romè, V. The byzantine fresco of Dormitio Virginis (12th century): diagnosis and conservation by means of innovative materials. *Technart 2015* Conference*: Non-destructive and microanalytical techniques in art and cultural heritage*. Catania (Italy), April 27–30, 2015

[91] Dei, L., Salvadori, B. Nanotechnology in cultural heritage conservation: nanometric slaked lime saves architectonic and artistic surfaces from decay.*Journal of cultural Heritage, 7*.2 (2006), 110-115.

[92] D'Armada, P., Hirst E. Nano-lime for consolidation of plaster and stone, *Journal of architectural conservation,* 18.1, (2012), 63-80.

[93] Daniele, V., Taglieri G. Nanolime suspensions applied on natural lithotypes: the influence of concentration and residual water content on carbonatation process and on treatment effectiveness. Journal of Cultural Heritage, 11.1 (2010), 102-106.

[94] Ruffolo S. A., La Russa M. F., Aloise P., Belfiore C. M., Macchia A., Pezzino A., Crisci G. M. Efficacy of nanolime in restoration procedures of salt weathered limestone rock Applied Physics A 114.3 (2014), 753-758

[95] Giorgi, R., et al. Nanoparticles of Mg $(OH)_2$: synthesis and application to paper conservation, *Langmuir*, 21.18 (2005), 8495-8501.

[96] Giorgi R., Dei L., Ceccato M. et al "Nanotechnologies for conservation of cultural heritage: paper and canvas deacidification." *Langmuir,* 18.21 (2002), 8198-8203.

it works very well as an alkaline reserve and does not originate any undesirable side products[97,98]. One of the most famous and lucky examples of their application is the Vasa warship[99] that represents a unique case in the study of ancient waterlogged wood and a challenge for finding new methods for artifacts conservation. The efficacy of nanolime on the deacidification of paper and canvas has been investigated by several authors. Some of them successfully used nanolime for the deacidification of paper containing iron gall ink, in fact the solvent, short chain alcohols mixtures, are highly compatible with components of the inks so that no bleeding are expected and Authors found that nanolime improved mechanical properties of paper and protected iron gall inked areas from discoloration during artificial aging[100,101].

It is well known that the efficiency of the treatment depends on nanolime morphology and size distribution, therefore the interest on different methodologies of synthesis arises from the fine control that can be achieved on particles size as well as on their morphology by choosing properly a synthetic strategy. Thus, an efficient methodology of synthesis requires a good mixing of the starting materials and chemical homogeneity of products. Several methodologies of synthesis of $Ca(OH)_2$ nanoparticles have been developed such as solvothermal[102], in homogeneous phase[103], micelles assisted[104], microemulsion water/oil assisted[105] or sol-gel[106]. However, most of these methods are very sophisticated, time consuming and expensive and a series of manipulations are necessary thus introducing impurities.

During the PhD research activity a new method for nanolime preparation by insolubilisation-precipitation has been devised with the aim of preparing nanolime dispersions whose particles have

[97] Bogaard, J., Whitmore P. M.. Effects of dilute calcium washing treatments on paper, *Journal of the American Institute for Conservation*, 40.2, (2001), 105-123.
[98] Lienardy, A., Van Damme P. Practical deacidification, *Restaurator*, 11.1 (1990), 1-21.
[99] Giorgi, R., Chelazzi D., Baglioni P., Nanoparticles of calcium hydroxide for wood conservation. The deacidification of the Vasa warship, *Langmuir*, 21.23 (2005), 10743-10748.
[100] Poggi, G., Giorgi, R., Toccafondi, N. et al. Hydroxide nanoparticles for deacidification and concomitant inhibition of iron-gall ink corrosion of paper, *Langmuir*, 26.24 (2010), 19084–19090.
[101] Poggi, G., Baglioni, P., Giorgi, R., Alkaline earth hydroxide nanoparticles for the inhibition of metal gall ink corrosion, *Restaurator*, 32 (2011), 247–273
[102] Poggi, G., Toccafondi, N., Chelazzi, D., Canton, P., Giorgi, R., Baglioni, P. Calcium Hydroxide Nanoparticles from Solvothermal Reaction for the Deacidification of Degraded Waterlogged Wood., *J. Colloid Interface Sci*., 473 (2016), 1–8.
[103] Poggi, G., et al. Calcium hydroxide nanoparticles for the conservation of cultural heritage: new formulations for the deacidification of cellulose-based artifacts, *Applied Physics A*, 114.3 (2014), 685-693.
[104] Taglieri, G., Mondelli, C., Daniele, V., Pusceddu, E., Scoccia, G. (2014). Synthesis, Textural and structural properties of calcium hydroxide nanoparticles in hydro-alcoholic suspension. *Advances in Materials Physics and Chemistry*, 4 (2014), 50-59.
[105] Nanni, A., Dei, L., $Ca(OH)_2$ Nanoparticles from W/O Microemulsions, *Langmuir*, 19 (2003), 933-938.
[106] Darčanova, O., Aldona B., Aivaras K. Sol–gel synthesis of calcium nanomaterial for paper conservation. C*hemija,* , 26.1 (2015), 25-31.

low polydispersity, low size and low agglomeration. At the same time, by simplifying the reaction conditions, a scale up of the synthesis can easily be foreseen.

This "insolubilisation-precipitation" method has not been proposed in literature for $Ca(OH)_2$ nanoparticles synthesis. It involves the preparation of an aqueous solution of calcium hydroxide at the solubility limit, to which a certain amount of 2-propanol is added thus causing the nanolime formation. The final hydroxide concentration is determined by the amount of saturated aqueous calcium hydroxide solution at a given temperature[107]. The main advantage of this method is due to the use of calcium hydroxide that, by alcohol addition, precipitates thus forming the nanolime dispersion in one step. Due to the low polarity of the solvent, the resulting alcoholic dispersion can be used on paper safer with respect to the corresponding saturated aqueous solution of calcium hydroxide.

The kinetic stability of the obtained dispersion was investigated by means of UV-vis Spectroscopy. The particle size, polydispersity, composition and crystal structure were investigated by means of Dynamic Light Scattering (DLS), Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDS) and Selected Area Electron Diffraction (SAED).

[107] Mellor J. W. A comprehensive treatise on inorganic and theoretical chemistry vol. III 1972, 677

## 3.2 Experimental Part

2-propanol and calcium hydroxide were supplied by Merck, Darmstadt, Germany, and were used without any further purification. Water was purified by a Millipore Organex system (R ≥ 18 MΩ cm) and de-carbonated by distillation on a substrate of potassium permanganate and sodium hydroxide (Sigma Aldrich).

The experimental apparatus used consists of a four necked flask connected to a six-bulb condenser, thermostated at 15 °C, to an optic-fibre thermometer, to a dropping funnel can and to a nitrogen tank to maintain the system under inert atmosphere. The flask is immersed in a bath of silicone oil at controlled temperature. The homogeneity of the dispersion is ensured by mechanical agitation via a magnetic stirrer.

Appropriate amounts of aqueous solutions of calcium hydroxide close to the solubility limit at 76 °C[108] were prepared by dissolving the appropriate quantity of the hydroxide in de-carbonated water. The solution concentration was 0.980 g/L.

In order to investigate the effect of temperature and of the amount of 2-propanol added, the synthesis was carried out in the range 40 - 76 °C and of 20-90 vol. % of alcohol.

Dispersions A, B and C were prepared at 40, 60 and 76 °C and alcohol amount of 90 vol. %, by adding dropwise the alcohol to an aliquot of the calcium hydroxide aqueous solution. The latter temperature has been selected once known that the boiling temperature of the azeotrope water/2-propanol mixture, whose composition is 12 vol. % in water, is 80.4 °C[108].

Once established the best temperature to obtain a stable dispersion, in order to evaluate the effect of the alcohol amount on the kinetic stability of the suspensions and morphology of nanolime dispersions, two samples were prepared at 76 °C with different alcohol amount, 20 and 50 vol. % respectively, by adding dropwise the alcohol to aliquots of the calcium hydroxide aqueous solution. These two samples were called E and D.

The synthesis has been performed at atmospheric pressure and at controlled temperatures as indicated above.

[108] Lebo R.B., Properties of Mixtures of Isopropyl Alcohol and Water, *J.Am.Chem.Soc.*, 43 (1921): 1005-1011

All prepared samples, whose composition is reported in Table 3.1, were analysed by turbidimetry and DLS. Samples C, D and E were investigated by TEM. Details on the instrumental set up are reported in appendix.

**Table 3.1.** Composition of the samples, calcium hydroxide and alcohol concentration and synthesis temperature. The error on the last digit is reported in parenthesis.

| **Sample** | **[$Ca(OH)_2$]** (mmol/L) | **[$Ca(OH)_2$]** (g/L) | **$C_{2\text{-propanol}}$** (vol. %) | **Synthesis temperature** (°C) |
|---|---|---|---|---|
| **A** | 1.43 (1) | 0.106 (1) | 90.0 (1) | 40 (1) |
| **B** | 1.41 (1) | 0.104 (1) | 90.0 (1) | 60 (1) |
| **C** | 1.40 (1) | 0.104 (1) | 90.0 (1) | 76 (1) |
| **D** | 7.49 (1) | 0.554 (1) | 20.0 (1) | 76 (1) |
| **E** | 4.34 (1) | 0.321 (1) | 50.0 (1) | 76 (1) |

The kinetic stability was evaluated by turbidimetric method[109] by computing the stability parameter $\xi = (A_t\text{-}A_\infty)/A_t$, as reported in the literature[110], where $A_t$ is the absorbance value of the dispersion at a given time and $A_\infty$ is the absorbance value at the end of the observations.

[109] Gabrielli, G., Cantale, F., Guarini, G. G. Adsorption of amphiphilic mixtures and stabilization of suspensions of hydrophobic solids in water, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *119*.2 (1996), 163-174.

[110] Ambrosi, M., Dei, L., Giorgi, R., Neto, C., Baglioni, P., Colloidal Particles of $Ca(OH)_2$: Properties and Applications to Restoration of Frescoes, *Langmuir*, 17 (2001), 4251-4255.

## 3.3 Results and discussion

*Effect of Temperature.* The ξ values obtained by turbidimetric measurements for A, B and C dispersions versus time are reported in figure 3.1.

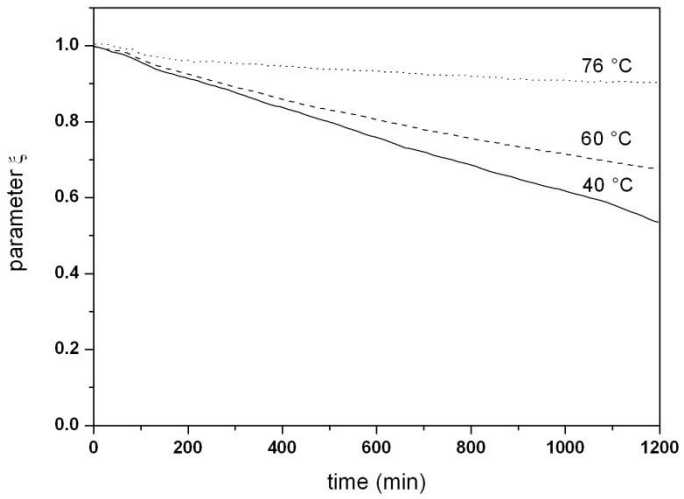


**Figure 3.1.** Parameter ξ vs. time for dispersions A, B and C obtained at 40, 60 and 76 °C, respectively.

All the dispersions showed a decrease in ξ as a function of time. In particular, the kinetic stability is higher for the sample C that was synthesised at higher temperature.

According to Fratini et al.[111] the kinetic stability depends on the particle size and on the dielectric constant of the medium, which affect the charge screening among particles. By considering the dielectric constant decrease with temperature[112], it is expected that nanoparticles dispersions prepared at lower temperature should result to be more stable, in opposition with the experimental finding. In order to rationalize the above observation, a DLS investigation was carried out. As an example, the correlation function C(τ) of C dispersion is reported in figure 3.2 (a).

[111] Fratini, E., Page, M. G., Giorgi, R., Cölfen, H., Baglioni, P., Demé, B., Zemb, T., Competitive surface adsorption of solvent molecules and compactness of agglomeration in calcium hydroxide nanoparticles. *Langmuir*, *23*.5 (2007), 2330-2338.

[112] Akerlof, G. Dielectric constants of some organic solvent-water mixtures at various temperatures. *Journal of the American Chemical Society*, 54.11 (1932), 4125-4139.

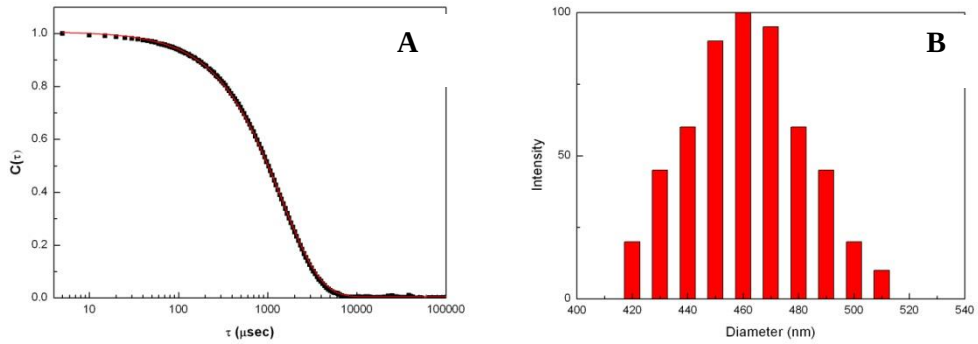


**Figure 3.2.** (a) The correlation function C(τ) vs. τ of the C dispersion accumulated for 10 min (point: experimental data, line: best fit). (b) the particle size distribution.

The points represent experimental data accumulated for 10 min., the solid line represents the best fit obtained by using the CONTIN method[113]. The computed function is in fair good agreement with the experimental data. The particle size distribution derived from the above method is reported in figure 3.2 (b). The mean particles hydrodynamic diameter is 461 nm with a low degree of polydispersity.

The hydrodynamic diameter (Dh) values and the relative variance (Rel. Var.) for the analysed samples are reported in table 3.2.

[113] Berne, B.J., Pecora, R., Dynamic Light Scattering, Wiley, New York (1976) ISBN: 0-486-41155-9.

**Table 3.2.** Hydrodynamic diameter (Dh), relative variance (Rel. Var.) of dispersion A, B and C.

| Dispersion | Dh (nm) | Rel. var. |
|---|---|---|
| **A** | 1320 | 1.98 |
| **B** | 823 | 1.64 |
| **C** | 461 | 0.07 |
| **D** | 241 | 1.43 |
| **E** | 317 | 1.58 |

Results clearly indicate that the lower stability observed at lower temperature must be ascribed to the formation of bigger and polydisperse particles. This is consistent with the higher solubility of $Ca(OH)_2$ at lower temperature[114]. On the basis of literature[115], the formation of nanoparticles in solution is the result of the nucleation and growth processes. The competition between the two processes can be rationalized on the basis of the La Mer model[116]. To obtain a monodisperse sample, the stage of nucleation must be as short as possible in such a way to allow a simultaneous formation of all nuclei and well separated from the stage of growth. Being the solubility of $Ca(OH)_2$ lower at higher temperature, it implies that in these conditions the nucleation stage is faster as compared to lower temperatures and better separated from the growth process thus bringing to the formation of roughly monodisperse particles.

*Effect of alcohol amount*. Values of $\xi$ as a function of the time for the C, D and E dispersions are reported in figure 3.3.

[114] Ali S., Ali A.S., Determination of Thermodynamic Parameters from the Dissolution of Calcium Hydroxide in Mixed Solvent Systems by pH-Metric Method, *J. Phys. Chem. Biophys*., 3.116(2013).
[115] Bonini, M., Baglioni, P., Chelazzi, D., Nanoscience for the Conservation of Works of Art, *Nanoscience Nanotechnology*, 28.315(2013).
[116] LaMer, V. K., Dinegar, R. H., Theory, production and mechanism of formation of monodispersed hydrosols, *Journal of the American Chemical Society*, *72*.11 (1950): 4847-4854.

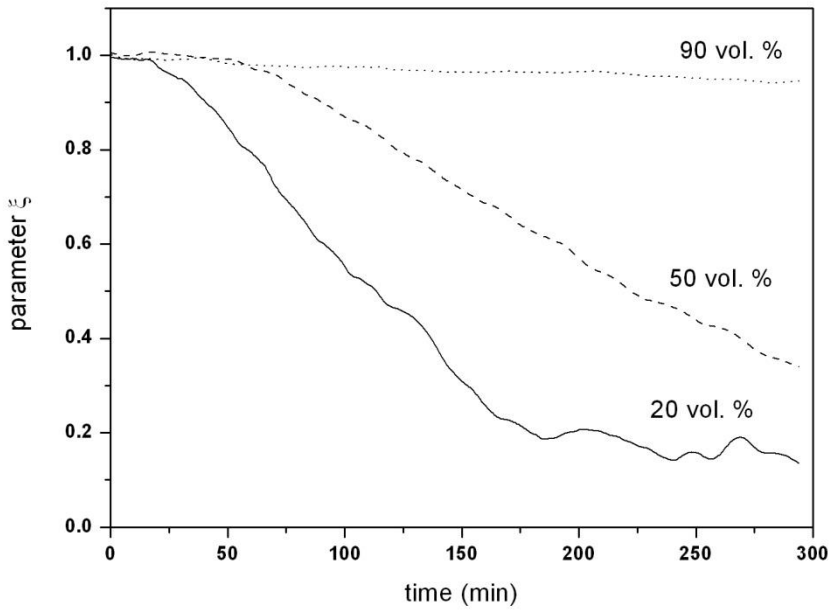


**Figure 3.3.** Parameter ξ vs. time. Sample C: dotted line; sample D: dashed line; sample E: continuous line.

The kinetic stability increases on increasing the alcohol content. Even by accounting that the overall calcium hydroxide concentration is in the order D > E > C, the observed variation on the stability cannot be ascribed exclusively to the different nanoparticles amount in the dispersions. Therefore, the above observation can be rationalized on the same basis of the effect of temperature. In fact, on increasing the alcohol content the dielectric constant reduces thus inducing a more stable dispersion. Moreover, the solubility of $Ca(OH)_2$ reduces thus, on the basis of the above considerations, promoting the formation of smaller particles.

In order to investigate the effect of particles size on the kinetic stability, a DLS investigation was carried out on sample D and E. The hydrodynamic diameter (Dh) values and the relative variance (Rel. Var.) for the analysed samples are reported in table 3.2. Results indicate that on increasing the alcohol amount (D < E < C) the hydrodynamic diameter increases but the particles synthesised at lower alcohol amount resulted polydisperse.

Therefore, the morphology of the particles was investigated by TEM. Micrographs at different magnifications of dispersions C, D and E are reported in figure 3.4.

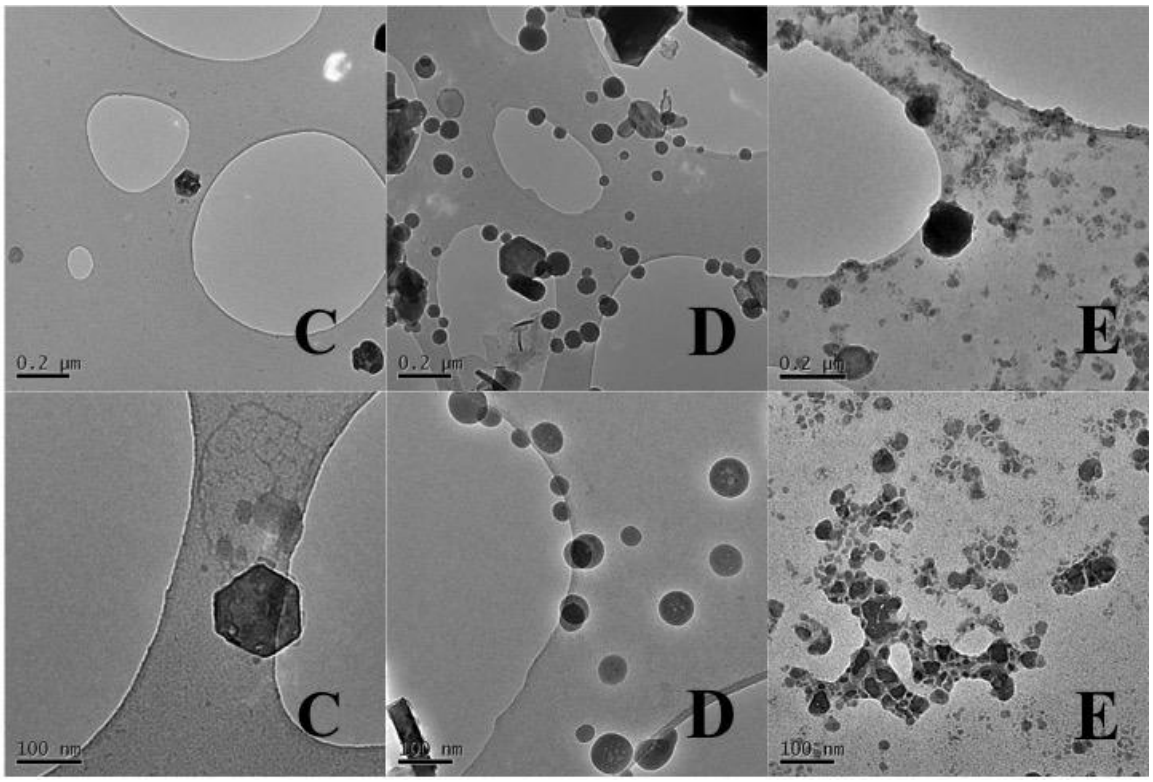


**Figure 3.4.** TEM micrographs of C, D and E dispersions at different magnifications.

The micrographs show that the nanoparticles in the dispersion C have a hexagonal shape with size of about 150 nm and are not aggregated. The identified hexagonal shape is typical of crystals of calcium hydroxide, as reported in literature[94] although some authors have reported the presence of nanolime needle-like[117] and cubic[118]. The size inferred from TEM micrographs is smaller than that evaluated by DLS for the same samples. As it is well known, DLS evaluates the diffusion of particles bearing their solvation shells.

The nanoparticles in the dispersion D have three shapes. Most of them are spherical, not aggregated and have size between 35 and 130 nm, some particles are hexagonal or rectangular with an average size of about 120 and 200 nm, respectively.

The nanoparticles in the dispersion E have an irregular spheroidal shape with a high degree of polydispersity and are aggregated. The particles size ranges from 7 to 37 nm and the size of the agglomerates is bigger than 100 nm.

[117] Valeria, D., Taglieri, G., Synthesis of Ca (OH) 2 nanoparticles with the addition of Triton X-100. Protective treatments on natural stones: Preliminary results. *Journal of Cultural Heritage, ,* 13.1 (2012):40-46.
[118] Rodriguez-Navarro C., Ruiz-Agudo E., Ortega-Huertas M., Hansen E., Nanostructure and Irreversible Colloidal Behavior of Ca(OH)2: Implications in Cultural Heritage Conservation, Langmuir, 21.24 (2005): 10948-10957.

The above is the first experimental evidence of spherical nanoparticles formation in solution. In fact, Liu et al.[119] have already synthetized spherical nanolime particles by hydrogen plasma-metal reaction method. The resulting porous nanoparticles had a mean size of 100 nm with a poly-nanocrystalline structure. The mean size of the nanoparticles here obtained is in line with those of the literature even if they are not porous. It cannot be excluded the conversion of Ca hydroxide particles in Ca-isopropoxide. Navarro[120] reported partial transformation of the hexagonal platelike portlandite crystals into pseudomorphs made up of an amorphous Ca-alkoxide phase, this process could bring to irregular spheroidal nanoparticles.

In order to exclude the presence of contaminants and to know the crystalline structure of nanoparticles, the composition and the structure were checked by EDS and by SAED, respectively.

The EDS spectra show peaks of calcium and oxygen from the analysed samples and copper and carbon from the grid used for TEM measurements. The latter element could derive also from some carbonation of sample during the synthesis or the manipulation. The SAED patterns are superimposable for the three investigated samples. Thus indicating that, independently from the particle shape, the crystalline structure is *Portlandite*, $Ca(OH)_2$.

As an example, EDS spectrum and SAED pattern of dispersion E are reported in figure 3.5.

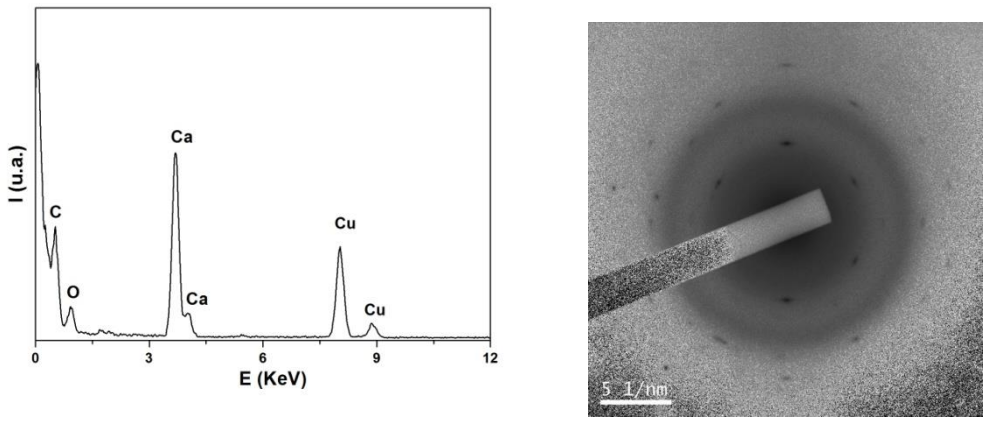


**Figure 3.5.** EDS spectrum (left) and SAED pattern (right) of dispersion E.

[119] Liu, T., Zhu, Y., Zhang, X., Zhang, T., Zhang, T., & Li, X. Synthesis and characterization of calcium hydroxide nanoparticles by hydrogen plasma-metal reaction method, *Materials Letters*, 64.23 (2010), 2575-2577.
[120] Carlos Rodriguez-Navarro, Irene Vettori, and Encarnacion Ruiz-Agudo, Kinetics and Mechanism of Calcium Hydroxide Conversion into Calcium Alkoxides: Implications in Heritage Conservation Using Nanolimes, Langmuir, 32 (2016), 5183−5194

The above findings clearly demonstrate that the alcohol amount affects both the kinetic stability and the particles size and morphology. This could be ascribed to the decrease in solubility of $Ca(OH)_2$ on passing from the system at 20% of alcohol to the one at 90%. The higher solubility favours a slower nucleation process not well separated from the growth, thus forming polydispersed particles that, as a consequence of electrostatic factors (higher dielectric constant), agglomerate and undergo a sedimentation process. On increasing of the alcohol amount, the solubility decreases thus favouring a faster nucleation well separated from the growth process. The almost monodispersed particles are stably dispersed in the medium mainly as a consequence of electrostatic factors.

# *CHAPTER IV*

# *A NEW SYSTEM FOR THE SIMULTANEOUS DEACIDIFYING AND REDUCTION OF ANCIENT PAPER*

## 4.1 Introduction

As can be inferred from the short review in Chapter I, paper degradation is a tricky phenomenon originating from both biotic and abiotic factors, internal and external. The understanding of history, use, structure, chemical composition, causes and mechanism of degradation is helpful in overcoming the conservation challenges of inhibiting further degradation and in choosing the conservation treatments and methods appropriate.

Based on literature evidences, up to now the inhibition of oxidation processes by conservation procedures and their long-term effects are still neglected.

An interesting option, already discussed in Chapter II, for paper conservation is the simultaneous use of deacidification and reduction treatment. This approach has been already proposed and applied by Bicchieri et al.[71,72 ,73] who experimented TBAB in the presence of calcium propionate and demonstrated the goodness of the treatment.

On these bases, the possibility of developing a method of simultaneous deacidification – reduction with the use of a dispersion of TBAB and calcium hydroxide nanoparticles in 2-propanol has been devised. The main advantage of using nanoparticles rather than calcium propionate arises from the opportunity to generate an alkaline reserve against further degradation.

To explore this possibility, the method has been set up on laboratory specimens. Ten sets of specimens were prepared, four made of cellulose, four made of cellulose with iron gall ink and two of lignin paper:

- Cellulose specimens:
    - artificially aged
    - oxidized and then artificially aged
    - oxidized, treated and then artificially aged to assess the long-term effects

- oxidized, artificially aged and then treated to assess the efficiency of the treatment on seriously damaged paper.

The same treatments have been applied to the inked cellulose specimens.

- Lignin paper specimens:
  - artificially aged
  - treated and then artificially aged in order to assess the long term efficiency.

For each set of specimens, physical and chemical parameters such as the surface pH, the degree of cellulose oxidation and the degree of polymerization (DP) were measured and used as gauges of the effectiveness of the proposed treatment. The microfadeometry was applied in order to evaluate the efficacy of the method in preventing yellowing of the treated samples due to light exposure of oxidized paper. This allowed estimating the resistance of the treated paper to aging induced by light. In addition, for lignin paper specimens, the mechanical measurements of tensile strength have been carried out.

## 4.2 Experimental part

2-propanol and calcium hydroxide were supplied by Merck, Darmstadt, Germany, and were used without any further purification. Water was purified by a Millipore Organex system (R ≥ 18 MΩ cm) and de-carbonated by distillation on a substrate of potassium permanganate and sodium hydroxide (Sigma Aldrich).

Cellulose Whatman n.1 paper (88.$gm^{-2}$, diameter of 90 mm) was supplied by Whatman®.

The 'Paper 3' (P3) was obtained from TNO (Center for Paper and Board Research), Delft (Netherlands). The fiber composition is 75 wt. % of ground wood and 25 wt. % of bleached sulfite softwood pulp. Kaolin (c.a. 20 wt. %) and alum–rosin are filler and sizing materials, respectively. The pH of the cold paper extract is 5.9, thus the alkaline reserve of this paper is zero[121].

The iron gall ink was prepared by mixing iron(II) sulfate and gall acid solutions both at a concentration of 0.045 mol/L. The preparation procedure is as follows:

- 1.22 g of gall acid was weighed on analytical balance (precision of 0.0001 g) and added to a beaker containing 140 mL of distilled water, measured by a graduate pipette (precision 0.1 mL). Then the suspension was stirred until forming homogenous solution of gall acid.

- 2 g of iron(II) sulfate was weighted and added to a beaker holding 10 mL of distilled water, measured by a graduate pipette (precision 0.05 mL).

- the iron(II) sulfate solution was added to the gall acid solution. The resulting solution immediately turned to blue-black color thus indicating the formation of iron(II) gall complex. Then the ink was left for 7 days in open vessel in order to allow sedimentation of particles in suspensions.

The system for simultaneous deacidification and reduction was prepared as follows. Calcium hydroxide nanoparticles were synthesized by insolubilisation-precipitation method as described in Chapter III. TBAB was added to the nanolime dispersion in order to obtain a nanolime concentration of 0.05 wt. % and a TBAB concentration of 0.875 wt. %.

40 specimens of Whatman® filter paper were treated as follows.

[121] Havermans, J. "Effects of air pollutants on the accelerated ageing of cellulose-based materials." *Restaurator* 16.4 (1995): 209-233.

5 specimens were left as received to be used as reference. These pristine specimens were labeled as "**B**".

20 specimens were inked with the model iron gall ink. A drop of 10 µL of a solution of iron(II) sulfate and gall acid 0.045 mol/L was deposited on 8 spots. These inked samples were labeled as "**+IG**"

30 specimens, 15 as received and 15 already inked, were oxidized by immersing them in a $KIO_4$ 0.015 mol/L aqueous solution for 15 min. Subsequently, they were washed with deionized water for 15 min. and then dried over a tray for 4 days. These artificially oxidized samples were labeled as "**O**".

The deacidification - reduction treatment was performed by soaking 12 oxidized specimens into 20 g of the TBAB-nanolime dispersion for 1 h then samples were dried over a tray for 1 day. Specimens that underwent this treatment were labeled as "**R**".

32 specimens were placed in a climatic chamber set at controlled temperature (80 °C) and relative humidity (65 %RH)[122]. The specimens were monitored after 7, 14, 21 and 28 days. The number of aging days is indicated with the label **[X]**. The specimens not artificially aged were labeled as **[0].**

8 of the oxidized samples, in details the ones aged for 7, 14, 21, 28 days underwent the same deacidification – reduction procedure as above described.

The schematic representation of the treated specimens is summarized in table 4.1 and table 4.2.

Two sets of 5 specimens of paper P3 were prepared. Four samples of the first set were artificially aged for 7, 14, 21, 28 days. The second set underwent the same deacidification – reduction procedure previously described for the cellulose samples. Four samples of the so-treated paper were artificially aged for 7, 14, 21, 28 days. The schematic representation of the treated specimens is summarized in table 4.3.

[122] ISO 5630-3:1986, Accelerated ageing of paper and board. Method for moist heat treatment at 80°C and 65% relative humidity

**Table 4.1.** Schematic representation of treated specimens of Whatman paper.

| | | | | | |
|---|---|---|---|---|---|
| B[0] | B[7] | B[14] | B[21] | B[28] | Untreated samples artificially aged for [X] days |
| O[0] | O[7] | O[14] | O[21] | O[28] | Oxidized with $KIO_4$ then artificially aged for [X] days |
| O[0]R | O[7]R | O[14]R | O[21]R | O[28]R | Oxidized with $KIO_4$ then artificially aged for [X] days, then reduced and deacidificated with TBAB-nanolime system |
| OR[0] | OR[7] | OR[14] | OR[21] | OR[28] | Oxidized with $KIO_4$, then reduced and deacidificated with TBAB-nanolime system, then artificially aged for [X] days |

**Table 4.2.** Schematic representation of treated specimens of Whatman paper inked with iron gall ink.

| | | | | | |
|---|---|---|---|---|---|
| B[0]+IG | B[7]+IG | B[14]+IG | B[21]+IG | B[28]+IG | Untreated samples artificially aged for [X] days |
| O[0]+IG | O[7]+IG | O[14]+IG | O[21]+IG | O[28]+IG | Oxidized with KIO4 then artificially aged for [X] days |
| O[0]R+IG | O[7]R+IG | O[14]R+IG | O[21]R+IG | O[28]R+IG | Oxidized with KIO4 then artificially aged for [X] days, then reduced and deacidificated with TBAB-nanolime system |
| OR[0]+IG | OR[7]+IG | OR[14]+IG | OR[21]+IG | OR[28]+IG | Oxidized with $KIO_4$, then reduced and deacidificated with TBAB-nanolime system, then artificially aged for [X] days |

**Table 4.3.** Schematic representation of treated specimens of P3 paper.

| | | | | | |
|---|---|---|---|---|---|
| P3[0] | P3[7] | P3 [14] | P3 [21] | P3 [28] | Untreated samples artificially aged for [X] days |
| P3R[0] | P3R[7] | P3R[14] | P3R[21] | P3R[28] | reduced and deacidificated with TBAB-nanolime system then artificially aged for [X] days |

## 4.3 Results and discussion

The pH values give information about the effectiveness of the chosen treatment. To achieve the effective treatment, the subject literature[1,2, 123 , 124] recommends the pH values drop within the optimum region from 6.2 to 8.5 at which both cellulose and lignin are stable. Otherwise, more acidic or alkaline pH values cause acidic or alkaline degradation of paper.

pH values, measured on both pristine and treated samples, as a function of artificial aging time are reported in figure 4.1. The shaded area highlights the ***optimum pH region*** mentioned above.

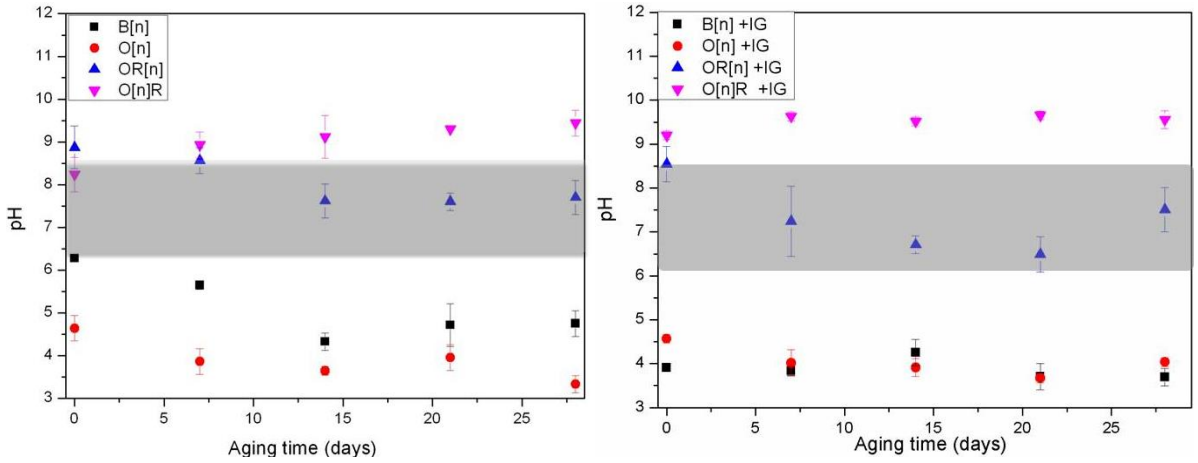


**Figure 4.1.** pH values vs. aging time. "pH optimum region" is indicated by the shaded area. The samples, indicated in the legend, underwent the treatment described in the text and summarized in tables 4.1 and 4.2.

Depending on the treatment, samples can be grouped on the basis of the measured pH. For all specimens, inked and not inked, the pristine samples as well as the oxidized ones have pH values in the acidic region (<6.2) and these values decrease with aging time for not inked samples and are substantially constant for inked samples.

The not inked and oxidized samples are characterized by more acidic pH values as compared with the pristine ones due to the increased number of –COOH groups in the cellulose. This is consistent

[123] Ahn K. et al.. "Sustainability of Mass Deacidification. Part I: Concept, Selection of Sample Books and pH-Determination". Restaurator, 32 (2011): 193–222
[124] Poggi, G., Baglioni, P. and Giorgi, R. et al.. "Alkaline Earth Hydroxide Nanoparticle for Inhibition of Metal Gall Ink Corrosion". Restaurator, 32 (2011):247–273

with the oxidation induced by periodate[81,125]. The oxidized functions can be considered as being responsible for the production of acidity on the basis of the kinetic model of paper degradation proposed in the literature[126]. The low pH values can facilitate further degradation of paper via an autocatalytic mechanism.[22]

Inked samples have lower pH values than the corresponding samples without iron gall ink and little differences are present between pristine and oxidized samples. Iron gall ink affects the stability of paper causing hydrolysis and oxidation[127] as a consequence of the catalytic effect induced by the metal ion through Fenton reactions at low pH.

Unlike the pristine samples, the treated samples have pH values falling in the basic region, thus indicating the efficacy of the treatment. Even for these samples the pH varies with the aging time, however, it can be considered constant, within the experimental error, for the samples aged prior to the deacidification – reduction treatment (O[X]R). This indicates that the efficiency of the proposed treatment is independent from the conservation state.

The results obtained for the samples treated preliminarily of artificial aging (OR[X]) indicate that the pH value is constant for one week of aging and then decreases with a trend similar to the one observed for the pristine samples. Notwithstanding that, the pH values are maintained within the optimal pH region, both for the inked and the not inked samples, thus indicating that the proposed method is efficient to prevent the natural paper acidification occurring with time. This could be interpreted by considering that the alkaline reserve is sufficient to slow down the acidic degradation up to one week of artificial aging.

[125] Durán, V. L., Larsson, A., and Wågberg L.. "On the relationship between fibre composition and material properties following periodate oxidation and borohydride reduction of lignocellulosic fibres." Cellulose, (2016):1-16.
[126] Calvini, P., Gorassini, A. and Merlani, A. L. “Autocatalytic Degradation of Cellulose Paper in Sealed Vessel“Restaurator, (2007):47–54
[127] Kolar, J., Strlič, M., “Iron Gall Inks: On Manufacture, Characterisation, Degradation and Stabilisation” National and University Library, 2006, ISBN 9616551191

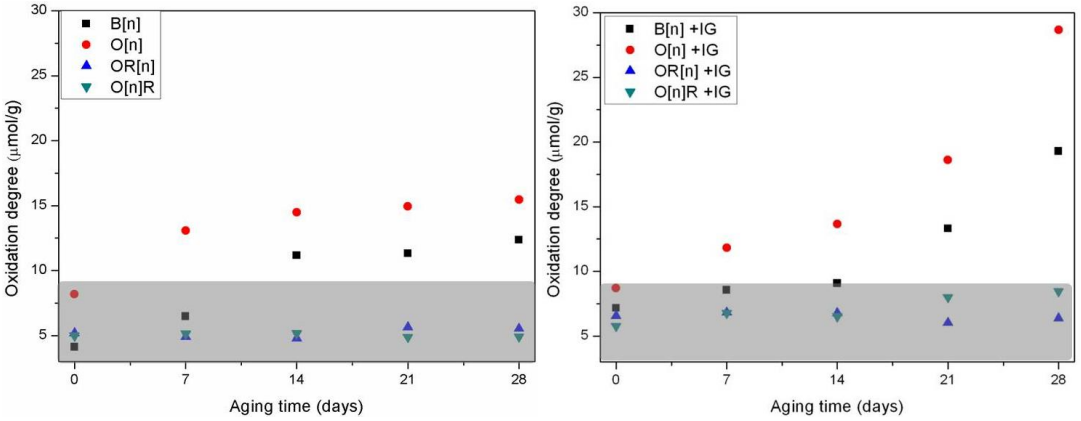


**Figure 4.2.** Oxidation degree (µmol/g) of paper as a function of aging time. The samples, indicated in the legend, underwent the treatment described in the text and summarized in tables 4.1 and 4.2. The shaded area highlights the *optimum carbonyl content region.*

The carbonyl content values, determined by the Szabolcs methodology[85], are shown as a function of the aging time in Figure 4.2.

Authors[3,4] recommend that the stable paper should have carbonyl content lower than 8 µmol/g. Based on this recommendation, samples were categorized into an ***optimum carbonyl content region*** and a ***high carbonyl content region***.

To achieve an effective treatment, the carbonyl content should be in the optimum carbonyl content region at which the paper is stable.

Based on the values determined on the pristine samples, the high value measured for the oxidized sample (9.5 µmol/g) is not surprising. The values determined for the two deacidified – reduced samples fall to c.a. 6.0 µmol/g close to that of the control paper, B[0], and within the upper control limit of the carbonyl content for good preservation of paper. This further confirms the efficacy of the proposed treatment.

The high carbonyl content region includes mostly of the results from the untreated samples. These results are in close agreement with those attained from pH measurements (***figure 4.1)*** thus confirming the action of oxidant and acidic environment. Moreover, by comparing the trend observed for the samples it clearly emerges that the pristine samples oxidize during the ageing similarly to those already oxidized. It is also worth noticing that the proposed treatment induces a resistance against oxidation that last over 28 days of the artificial aging. This result is particularly

interesting once known the relationship between the artificial aging under the conditions chosen and the natural aging at 23 °C and 50 %RH[61]. On this basis, for Whatman no. 1 paper, 7 days of artificial aging correspond to 10 years of natural aging with regard to paper oxidation state.

The samples exposed to iron gall ink were endangered more than those free from the ink as indicated by the carbonyl content values divergence. This could be ascribed to the catalyst action of Fe(II) ion[4].

The samples aged for 21 and 28 days before the deacidification – reduction treatment show higher values of carbonyl content than those reduced before aging. This result indicates that the treatment used was less effective on recovering the optimal conditions properly on paper heavily damaged probably as a consequence of the oxidative degradation brought by the high alkaline pH. Notwithstanding, these two values lie within the optimal carbonyl content region.

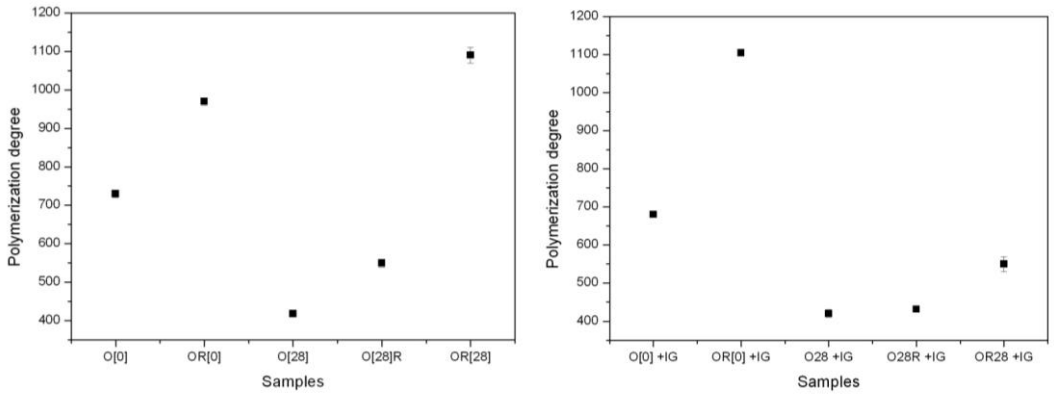


**Figure 4.3.** Degree of polymerization for some of the samples summarized in tables 4.1. and 4.2

The weighted average molecular mass (Mw) of cellulose was derived from SEC by using the procedure described by Lojewski[128]. The degree of polymerization (DP) has been calculated[129] from the ratio between Mw and Mg, where Mg is the molar mass of glucopyranose.

For not inked samples, the initial oxidized sample (O[0]) has a mean value of DP 730±10, unlike the sample first oxidized and treated OR[0] whose mean value equals 970±10. The treatment has

[128] Łojewski, T., et al. "Evaluating paper degradation progress. Cross-linking between chromatographic, spectroscopic and chemical results." Applied Physics A 100.3 (2010): 809-821.
[129] Calvini, P., Gorassini, A. and Merlani, A. L.. "On the kinetics of cellulose degradation: looking beyond the pseudo zero order rate equation." Cellulose 15.2 (2008): 193-203.

led to an increase in DP by 25%. More importantly, DP of the sample aged for 28 days (OR[28]) increased in comparison with the unaged counterpart (1090±20). It suggests that the artificial aging of the treated samples promotes further polymerization of cellulose.

The oxidized and artificially aged sample O[28] has a DP value of 418±7 thus indicating that it is in a poor conservation state. For this sample, the treatment increased the DP value by 31% (the value attained is 550±10).

The DP values of inked samples show the same qualitative trend. The initial oxidized samples (O[0]+IG) has a mean value of 680±7, the treated O[0]R+IG has 1104±7. These values indicate that the treatment in presence of iron gall ink lead an increment of 62% being so far more effective on this specimen than in that not inked. Also in this case the proposed treatment promotes polymerization during artificial aging.

The above findings can be explained by considering that the proposed treatment promotes a crosslinking or branching of cellulose chains. This crosslinking proceeds also during the artificial aging probably as a consequence of the chosen ageing conditions and can be favored by the presence of the metal ion.

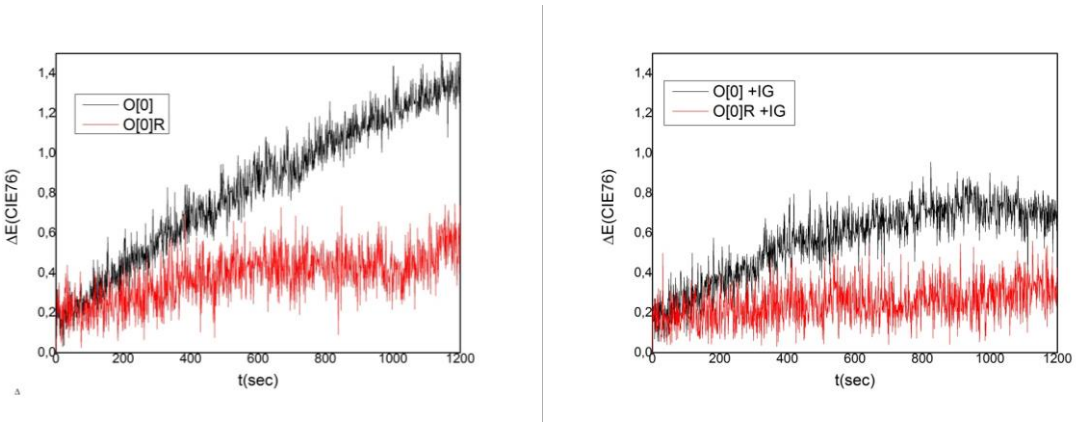


**Figure 4.4.** Microfadeometry test for sample O[0] and O[0]R

The color variation occurring under UV aging is reported as ΔE(CIE76) vs. time in figure 4.4 for the oxidized untreated and treated samples, respectively. A large difference in the yellowing rate for untreated and treated samples has been registered thus indicating the ability of the treatment in protecting the paper against chemical processes promoted by UV radiation.

Once established the effectiveness of the proposed treatment on pure cellulose specimens, it has been considered the effectiveness with regards to paper from wood pulp.

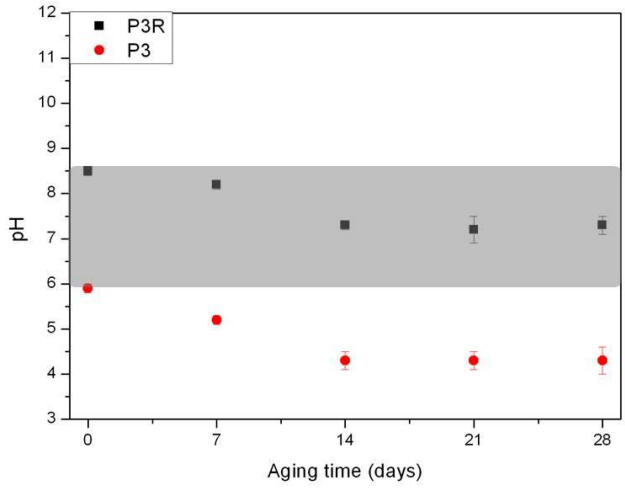


**Figure 4.5.** pH values vs. aging time. "pH optimum region" is indicated by shaded area. The samples, indicated in the legend, underwent the treatment described in the text and summarized in table 4.3.

P3 paper undergoes acid hydrolysis with artificial aging with a trend similar to the one observed for the cellulose samples. The proposed treatment is able to bring the pH value within the optimal pH region and to maintain it during the artificial aging, thus indicating that even on wooden pulp paper it prevents the natural paper acidification occurring with time.

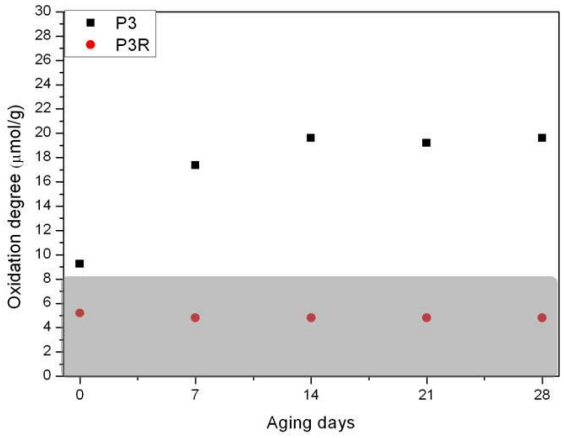


**Figure 4.6.** Oxidation degree (µmoles/g) of P3 samples as a function of aging time. The shaded area highlights the *optimum carbonyl content region.*

The carbonyl content values, determined by the Szabolcs methodology[85], are shown as a function of the aging time in Figure 4.6. P3 untreated samples show high values of carbonyl content. This result indicates a bad state of preservation of paper in close agreement with the information attained from pH measurements. P3 samples that underwent the deacidification – reduction treatment are characterized by a carbonyl content falling to c.a. 5.0 µmol/g thus confirming the efficiency of the treatment over the time even on lignin paper.

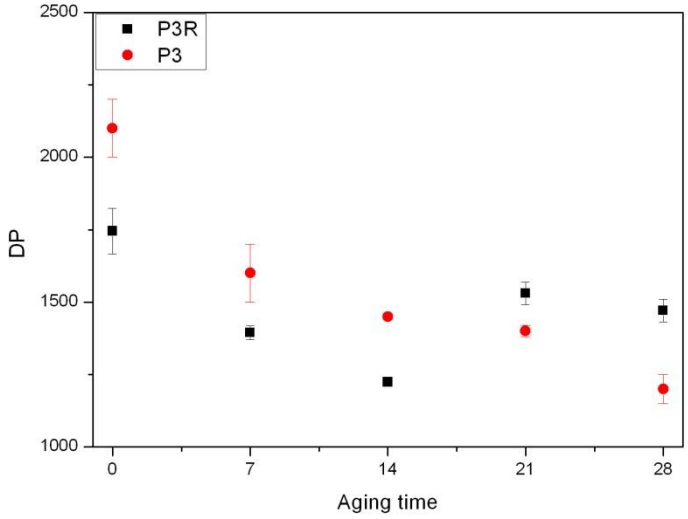


**Figure 4.7.** Degree of polymerization for samples summarized in table 4.3.

The degree of polymerization (DP) has been calculated as before from the ratio between Mw and Mg by taking into account for the presence of hemicelluloses[129,130].

The untreated paper P3 undergoes to a depolymerization with artificial aging with a rate that decreases on aging. For the treated and aged samples, the DP values tend to an increase after the initial fast decrease. This could be explained by considering that the proposed treatment reveals to be effective only on heavily damaged paper for which the DP is low. Moreover, by considering the pH values characterizing this paper it can be foreseen the positive effect of alkaline environment in promoting the crosslinking or branching of cellulose chains. This unexpected result deserves to be deepened and confirmed by other measurements of macroscopic properties directly depending on the DP.

[130] Łojewski, T., Zięba, K., Kołodziej, A., and Łojewska, J. Following cellulose depolymerization in paper: comparison of size exclusion chromatography techniques. *Cellulose, 18*.5 (2011): 1349-1363.

For this reason, mechanical measurements of tensile strength (according to standard TAPPI T231) have been carried out. Values of breaking length derived accordingly to the above method are reported in figure 4.8.

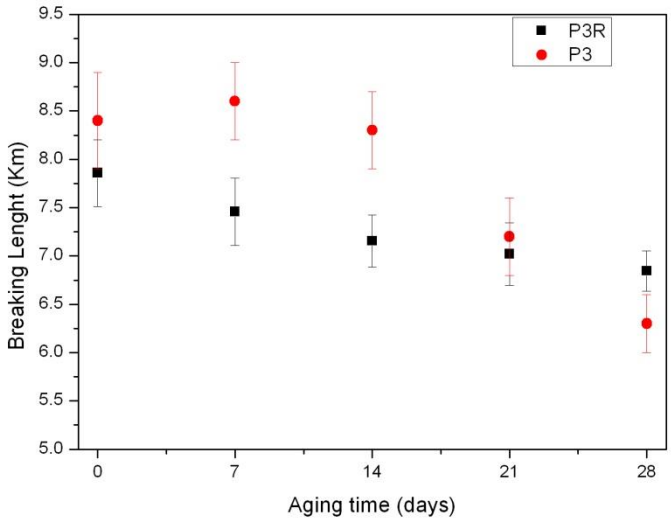


**Figure 4.8.** Breaking length versus aging time for samples summarized in table 4.3.

For the untreated and aged samples the observed trend is in fair good agreement with that reported in literature[131,132]. Generally, the breaking length value decreases with the paper aging after a short induction period probably due to the increased hydrogen bonds between cellulose molecules.

For treated and aged samples the values decrease without any induction period. It has been noted that the variation on the measured values is lesser for the treated samples. This, in our opinion, is a direct consequence of the crosslinking or branching between cellulose chains and further confirms the DP results. In fact, Wilson and Parks affirm[56] that the zero span should not be affected by the crosslinking except as a secondary effect of fiber degradation if crosslinking occurs due to the presence of an acid catalyst. Moreover, the breaking length of the treated paper tends to be higher for long aging time than that measured for the untreated one in agreement with the results of DP.

[131] Emsley, A. M., Heywood, R. J., Ali, M., and Eley, C. M.. On the kinetics of degradation of cellulose. *Cellulose*, *4*.1 (1997): 1-5.
[132] Emsley, A. M., Heywood, R. J., Ali, M., and Xiao, X. Degradation of cellulosic insulation in power transformers. 4. Effects of ageing on the tensile strength of paper. *IEE Proceedings-Science, Measurement and Technology*,*147*.6 (2000): 285-290.

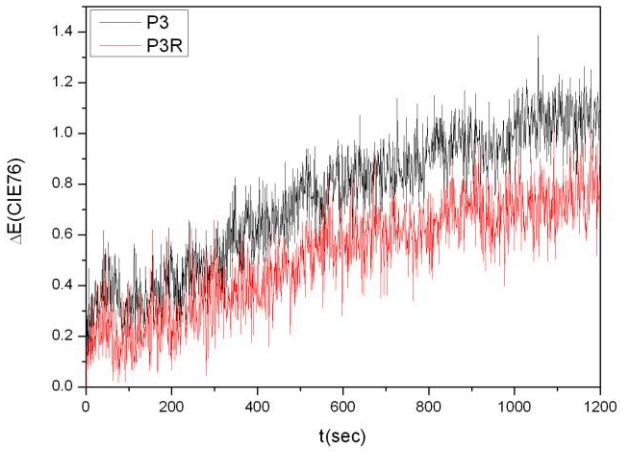


**Figure 4.9.** Microfadeometry test for sample P3 and P3R

The color variation occurring under UV aging of the untreated and treated P3 samples is reported as ΔE(CIE76) vs. time in figure 4.9. The small differences observed indicate that treatment has negligible effect in protecting the paper against UV radiation. This could be explained by considering that for lignin paper the oxidation leads to a paper discoloration through the formation of carbonyl groups in cellulose and chromophores in lignin (e.g. conjugated C=C, ortho- and/or para-quinones). It is already know that lignin inhibits self-oxidative degradation of cellulose[133]. Moreover, it has been reported that lignin oxidizes itself apparently suppressing the oxidation of cellulose to more oxidized forms (–COOH)[129]. Since TBAB is effective in reducing the carbonyl to alcohol function, in the P3 paper its effect is overcome by the chromophores formation in lignin.

[133] Barclay, L. Ross C., Xi, F. and Norris, J. "Antioxidant properties of phenolic lignin model compounds." Journal of wood chemistry and technology 17.1-2 (1997): 73-90.

# *CHAPTER V*

# *CASE STUDIES*

## 5.1 Introduction

***The Archive document belonging to Archivio Storico Diocesano of Palermo (Italy).***

This manuscript belonged to the fund of the parish of *San Giovanni degli Eremiti (Palermo)*, later absorbed by the *Archivio Storico Diocesano of Palermo*, to which it still belongs. The archival document concerns the sentences dictated by the Grand Court of the Archbishop of Palermo in the years 1642 and 1643. It is divided into two parts. The first part is an index for easy reference: the list is in alphabetical order and shows the names of those undergoing judgment, along with the page number. The second part of the book reports the actual judgments.

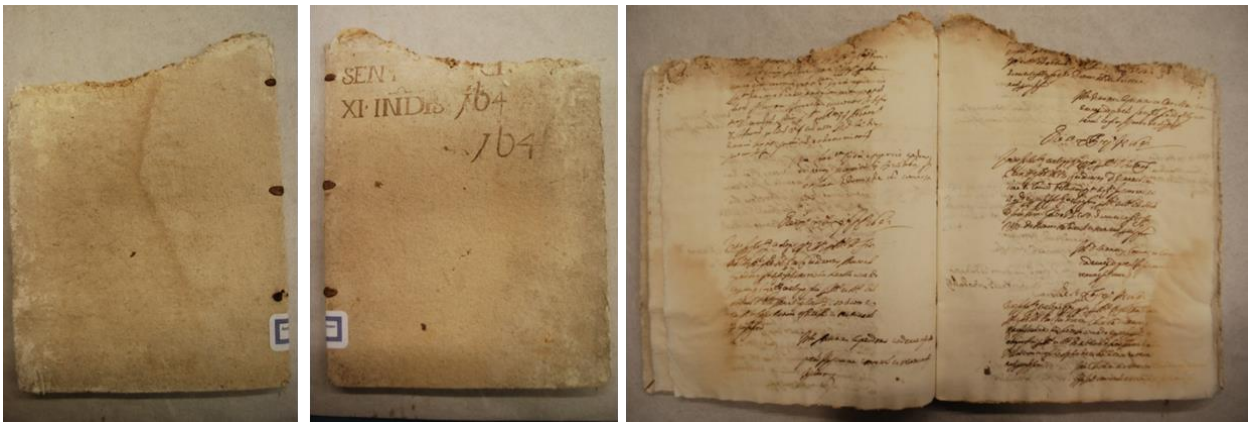


**Figure 5.1.** Archive document belonging to Archivio Storico Diocesano of Palermo (Italy).

***The four Gospels in Arabic and Latin belonging to Biblioteca Alagoniana of Syracusae (Italy)***

The book under study consists of the four Gospels in Arabic and Latin belonging to *Biblioteca Alagoniana* of Syracusae (Italy). The book was printed by the Medicean Tipography in 1591. The Edition is richly incised by Leonardo Sunshade and designed by Antonio Tempesta. The binding is not coeval (first quarter of the nineteenth century), it is rigid with cover in sheepskin, and pattern in blue marble type with fabric capitals and paper spine. The edition, particularly valuable, presents strong brownish papers with a significant tightening of dossiers for excessive sizing of the back. Moist spots are present and have caused an alteration of colours; several pages show a widespread browning. Superficial abrasions and a light insect attack are also present. The conservation status of the paper and the conditions of the binding determined the choice of the intervention with a complete restoration both of the papers and of the binding.

**Figure 5.2.** Four Gospels in Arabic and Latin belonging to Biblioteca Alagoniana of Syracusae (Italy)

***The Breviary of 19th century belonging to a private collection.***

The book under study consists in a Roman Breviary containing Italian liturgical rites of the Catholic Church translated from the Latin by Monsignor Martini and printed in 1880 by "Fratelli Sacchi Editori" (Milano, Italy). The book belongs to a private collection and presents pages with a widespread yellowing and brown stains. The binding is not coeval. It is rigid with cover in cardboard recovered with old sheets from a 20$^{th}$ newspaper.

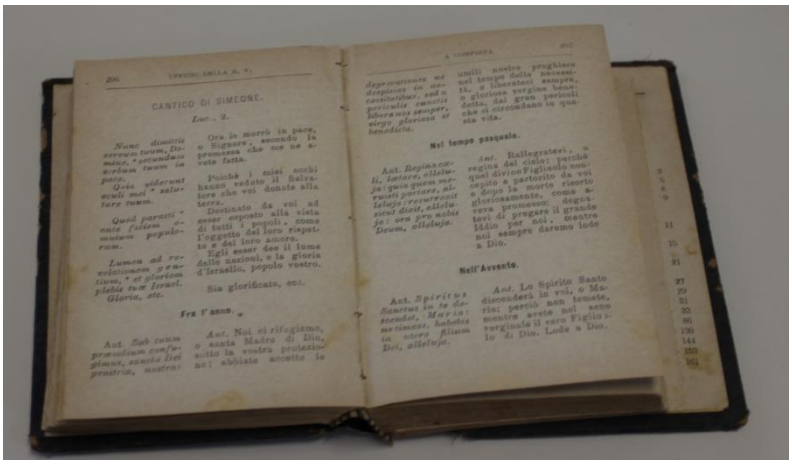


**Figure 5.3.** The printed book of 19th century belonging to a private collection

## 5.2 Preliminary characterization

***The Archive document belonging to Archivio Storico Diocesano of Palermo (Italy).***

From visual inspection, the Archive document belonging to *Archivio Storico Diocesano* resulted heavily damaged, in particular in the upper part. The top cut of the document has been completely lost, damaged by the water where it probably had remained immersed long enough to complete degradation and disintegration of the affected area. The sheets have, especially in the outer part of the page, large gore zones in which the water has dissolved part of the staining inks thus causing gaps in the text. Finally, there are holes due to the corrosive action of inks.

In order to choose the appropriate intervention treatment, a diagnostic survey on the book was prior performed in order to get information on the state of conservation. The surface pH, the nature of the ink and the conservation state of paper were characterized by using pHmetry, Raman and NMR Spectroscopy.

A typical $^{13}C$ {$^{1}H$} CP MAS NMR spectrum of the sample is reported in figure 5.4.

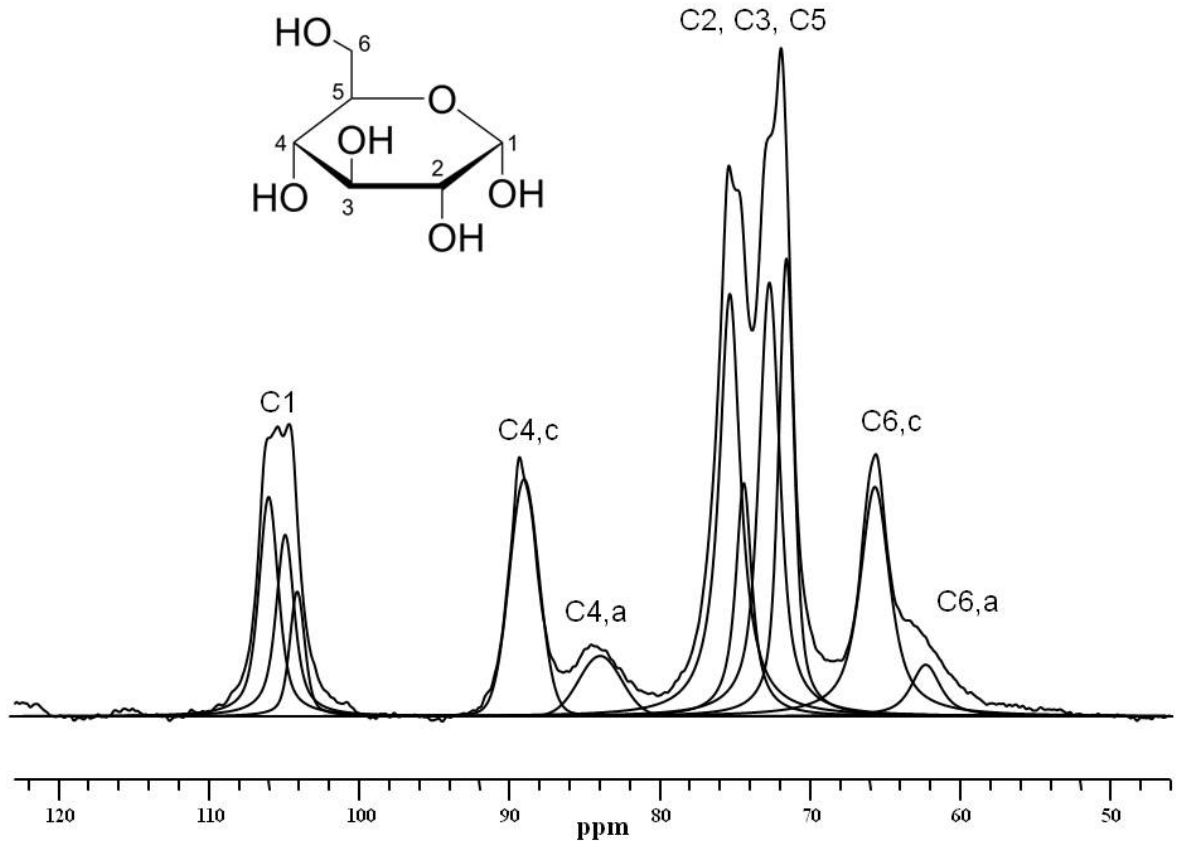


**Figure 5.4.** $^{13}C\{^{1}H\}$ CP MAS NMR spectrum of paper

Only the characteristic signals of the cellulose are present in the spectrum. This indicates that the paper is made from cloths[76]. All the chemical shifts were assigned following the literature[77]. An intense signal, assigned to C1, is observed in the range between 110 and 100 ppm. This signal is the convolution of three contributions due to the Iα and Iβ forms of cellulose. The signals at 88.7 and 83.8 ppm are due to the C4 of crystalline and amorphous cellulose, respectively. Peaks between 80 and 70 ppm are due to C2, C3 and C5 carbons. The signals at 67 and 63 ppm are due to C6 of crystalline and amorphous cellulose, respectively. It is well known from literature[134] that the conservation state of the paper is correlated to the crystallinity degree of the cellulose fibres. In fact, acid and bacterial degradation increase the crystallinity degree because the amorphous cellulose, more hydrophilic and thus sensitive to changes, is mostly hydrolysed with respect to the crystalline one. In order to deepen this aspect, the crystallinity degree was computed from the areas ratio of the signals at 88.77 and 84.4 ppm due to the C4 of amorphous and crystalline cellulose. Each area has been obtained by deconvolution of the signals by using the Levenberg - Marquardt algorithm, optimized with the Nelder - Mead method[13, 135]. The obtained degree of crystallinity is 71%, indicative of a paper in advanced state of deterioration. In fact, for cotton linter as well as for paper in good state of conservation a value of c.a. 60 % is reported[136].

In order to identify the nature of inks, Raman Spectroscopy has been applied. Spectra, acquired on several points of some bifolios, are similar. As an example, the Raman spectra of the inks of pages 12 and 83 are reported in figure 5.5.

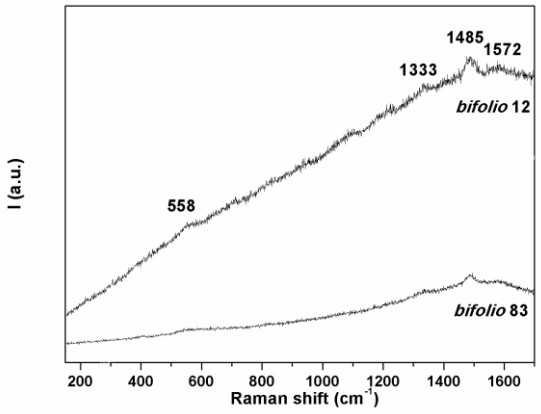


**Figure 5.5.** Raman spectra of black ink of bifoli 12 and 83.

[134] Attanasio, D., Capitani, D., Federici, C., Paci, M., Segre, A. L., Electron Paramagnetic Resonance and $^{1}H$ and $^{13}C$ NMR Study of Paper, *ACS Symposium Series*, 598(1995): 333
[135] Nelder, J. A., Mead, R. "A simplex method for function minimization. *The computer journal*", 7.4 (1965): 308-313.
[136] Spinella, A., Capitani, D., Bastone, S., Caponetti., E. "Solid state NMR to characterize paper and parchment samples from a 16th century book", Conservation Science for the Cultural Heritage, Ed. Springer, (2012): 208- 217

The spectra are disturbed by the fluorescence background due probably to organic compounds such as glue. The identification of the bands has been performed by comparison with database[137]. The observed bands have been ascribed to iron gall ink (peaks at 558 and 1485 $cm^{-1}$) and carbon black (peaks at 1572 and 1333 $cm^{-1}$), indicating that the used ink is a mixture of both the ancient inks. The harmful effects of iron gall inks on the carrier were scientifically confirmed[46]. When used on paper, this ink induces high damages, due to the presence of organic acid that leads to very acidic pH values and consequentially to cellulose acid hydrolysis, and to the presence of iron(II) that catalyzes cellulose oxidation.

In order to evaluate the acidity of the paper, pH measurements were performed in different unwritten zones of every bifolio. The obtained values were in the range 7-8, thus indicating that the paper is basic (see table 5.2). These values are probably consequence of the action of a possible alkaline reserve due to the presence of calcium carbonate added during the manufacturing of paper. Anyway, the pH values indicate a good state of conservation of the paper. However, as expected, according the nature of the identified inks, the pH values acquired on the inked part are lower by 1 unit than those acquired in the unwritten zones.

[137] http://www.chem.ucl.ac.uk/resources/raman/index.html

***The four Gospels in Arabic and Latin belonging to Biblioteca Alagoniana of Syracusae (Italy)***

In order to undertake a proper restoration intervention, the paper of the Four Gospels was characterized with several techniques such as surface pHmetry, micro-Raman, $^{13}C$ {$^{1}H$} CP-MAS NMR, FT-IR, and UV-Vis diffuse reflectance spectroscopies.

The surface pH was measured in various areas, both printed and not printed. The paper has acidic pH, with an average value of 5.5±0.4.

In order to identify the nature of inks, Raman Spectroscopy was applied. Spectra were acquired on several points of the book and are similar thus indicating that only one ink was used. As an example a spectrum is reported in figure 5.6.

The identification of the bands was performed by comparison with database [138]. The observed bands have been ascribed to carbon black (peaks at 1572 and 1333 $cm^{-1}$).

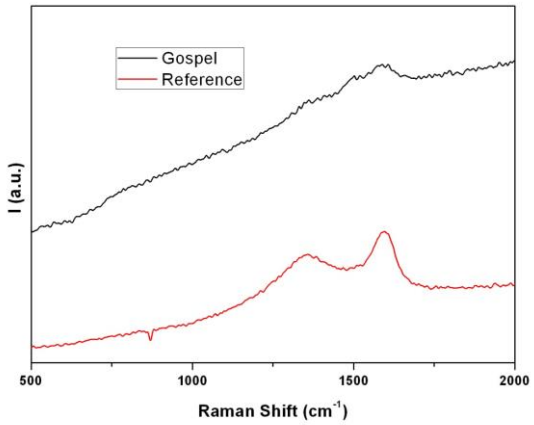


**Figure 5.6.** Raman Spectra of Ink (black), carbon black reference (red)

In order to characterize the nature and the state of conservation of the paper, $^{13}C$ {$^{1}H$} CP-MAS NMR spectra were acquired on several samples. No significant differences among them were observed. A representative spectrum is reported in figure 5.7.

[138] Bevilacqua N., Borgioli L., Adrover I. G., I Pigmenti nell'arte dalla preistoria alla rivoluzione industriale (Tal 26) 2010 - ISBN 978-88- 6336- 090-5.

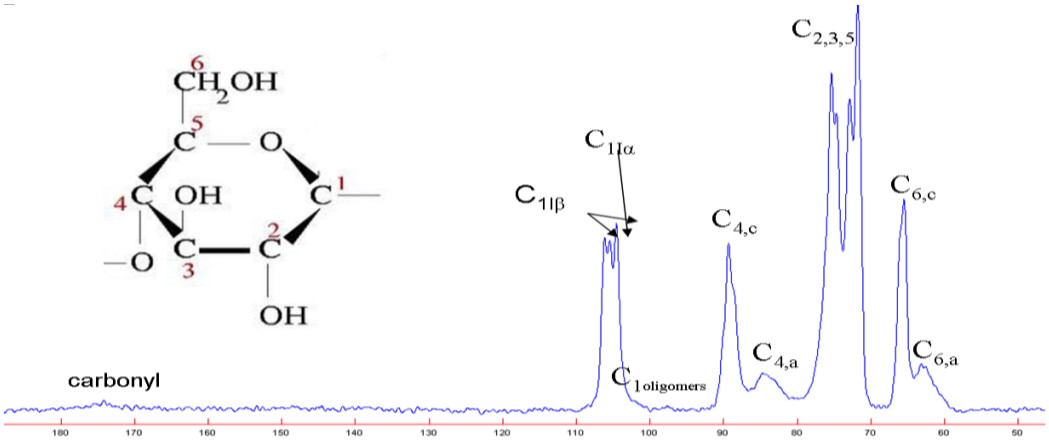


**Figure 5.7.** A representative $^{13}C\{^{1}H\}$ CP MAS NMR spectrum of the analysed paper

Only the characteristic signals of the cellulose are present in the spectrum. This indicates that the paper is made from cloths (cotton, linen)[76]. All the chemical shifts were assigned by following the literature[77] and accordingly to what already reported at page 61. The crystallinity degree was evaluated by following the procedure already described at page 61. The obtained value (55 %) indicates that the paper is in a good state of conservation in spite of the acidic pH value[13]. In addition, the spectrum has a great number of cellulose oligomers signals possibly originating from the hydrolysis of the glucosidic bonds. A carbonyl carbon signal due to cellulose oxidation can be observed but the signal to noise ratio is very low to perform a quantitative analysis.

In order to look closer at the oxidation state of the paper, FT-IR spectra were collected. A typical spectrum obtained is reported in figure 5.8. The bands attribution is complicated by the different cellulose structures that can coexist in paper. However, the carbonyl groups content was estimated by the *R-ratio* calculated from the ratio between area of the carbonyl band (1730 $cm^{-1}$) and that of CH stretching (2850-2950 $cm^{-1}$). Its value is 6.4, characteristic of oxidized paper thus confirming the oxidation of the paper[139].

139 Łojewska, J., Miśkowiec, P., Łojewski, T., & Proniewicz, L. M. (2005). Cellulose oxidative and hydrolytic degradation: In situ FTIR approach. Polymer degradation and stability, 88(3), 512-520.

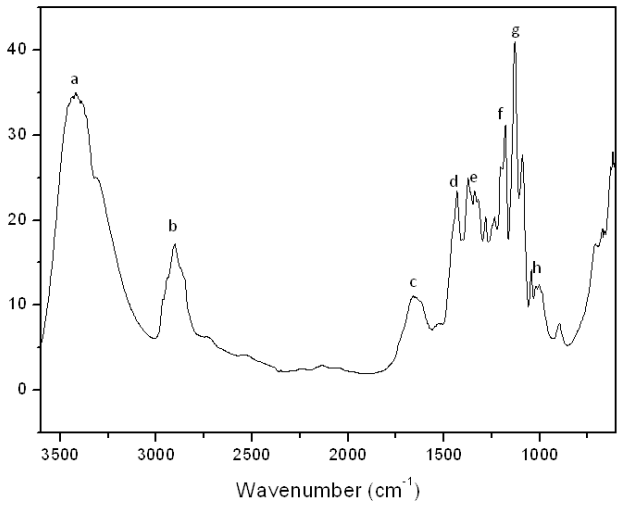


**Figure 5.8.** FT-IR spectrum of paper. The bands are assigned as a: ν(OH)free, b: ν(C-H), c: ν(C=O), d: δ(C-H); δ(C-OH), e: δ($CH_2$)wagging, f: ν (C-C)ring, g: ν(C-O-C)glycosidic, h:ν(C-OH)[140].

[140] Garside, P. and Wyeth P. "Identification of cellulosic fibres by FTIR spectroscopy-thread and single fibre analysis by attenuated total reflectance." Studies in Conservation 48.4 (2013): 269-275.

***The Breviary of 19th century belonging to a private collection.***

The paper of the Breviary was characterized with several techniques such as surface pHmetry, SEC, $^{13}C$ {$^{1}H$} CP-MAS NMR and UV-Vis diffuse reflectance spectroscopies in order to understand its state of conservation before carrying out an appropriate treatment for its conservation.

$^{13}C$ {$^{1}H$} CP-MAS NMR spectra were acquired on several samples in order to have information on state of conservation and on making processes of the paper. No significant differences among spectra were observed. A representative spectrum is reported in figure 5.9. The chemical shifts with the relative assignments are reported in table 5.1.

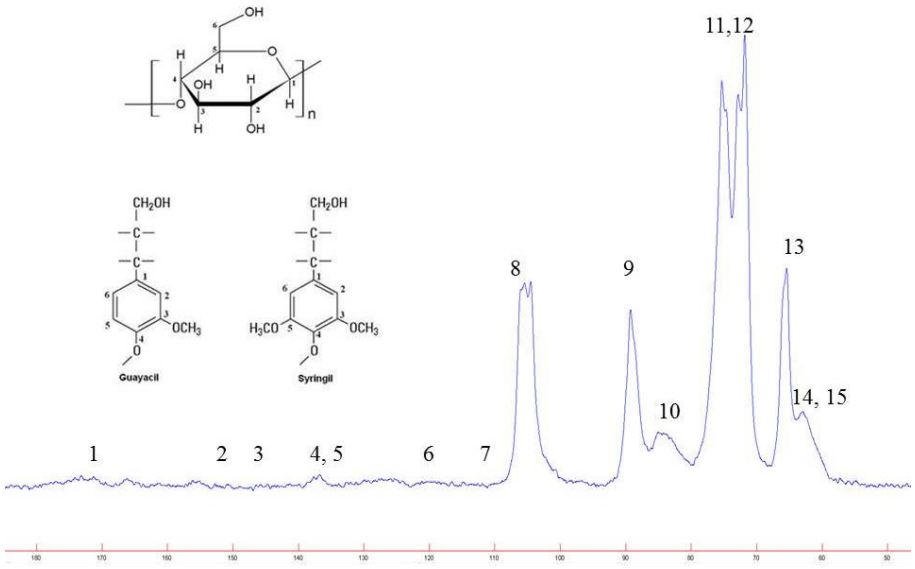


**Figure 5.9.** $^{13}C${$^{1}H$} CP MAS NMR of Breviary paper with a representation of the guaiacyl and syringyl units of the lignin and the monomeric unit of the cellulose. Peak attributions are reported in table 5.1.

**Table. 5.1.** Chemical shift assignments of the $^{13}C\{^{1}H\}$ CP MAS NMR spectrum of the sample R. S=syringyl, G=guaiacyl, e=etherified, ne=not etherified

| | ppm | Attribution | Assignment |
|---|---|---|---|
| 1 | 172 | -COO-R, CH3-COO- | Hemicellulose |
| 2 | 152 | S3(e), S5(e) | Lignin |
| 3 | 147 | S3(ne), S5(ne), G1, G4 | Lignin |
| 4 | 136 | S1(e), S4(e), G1(e) | Lignin |
| 5 | 134 | S1(e), S4(e), G1(e) | Lignin |
| 6 | 121 | S1(ne), S4(ne), G1(e) | Lignin |
| 7 | 114-106 | G5, G6, S2, S6 | Lignin |
| 8 | 105 | C1 | Cellulose |
| 9 | 89 | C4 (crystalline) | Cellulose |
| 10 | 84 | C4 (amorphous) | Cellulose |
| 11 | 75 | C2, C3, C5 | Cellulose |
| 12 | 72 | C2, C3, C5 | Cellulose |
| 13 | 65 | C6 | Cellulose |
| 14 | 57 | O-CH3 | Lignin |
| 15 | 55 | Cγ | Lignin |

The signal 1 is due to the carbonyl carbons of the hemicellulose. Signals 2-7 are the resonances of the aromatic carbons of the lignin. In particular signal 2 is due to the C3 and C5 of the etherified syringyl units forming the β-O-4 structures. The peak 4 is the resonance of the C4 of the etherified syringyl and guaiacyl units and of the C3 and C5 of the not etherified syringyl units. The syringyl and the guaiacyl structures are reported in figure 5.9. The signals 8-14 were attributed to the cellulose whose structure is reported in figure 5.9. The signals 9 and 10 are resonances of the C4 of the amorphous and crystalline cellulose respectively. The signal 15 is due to the methoxy groups of the lignin.

Being present in the spectra both the characteristic signals of cellulose and of lignin, this indicates that the paper is made from wood pulp. The crystallinity degree, calculated with the method previously explained (page 61), has a value of 60 %. Literature evidences indicate that for paper from cotton linter this value indicate a good state of conservation[137]. To our knowledge, no evidences are present about the correlation among crystallinity degree and state of conservation for cellulose from lignin paper. Thus from this finding it is not possible to have information about the hydrolysis occurred. Notwithstanding, the spectrum has signals of cellulose oligomers that are possibly originating from the hydrolysis of the glucosidic bonds. A carbonyl carbon signal due to cellulose oxidation can be observed but the signal to noise ratio is very low to perform a quantitative analysis.

In order to ascertain hydrolysis and oxidation degradation, the surface pH was measured and the oxidation of cellulose was evaluated by determining the carbonyl content paper accordingly to the Szabolcs methodology[85]. The surface pH was measured in various areas, both printed and not printed. The paper has acidic pH, with an average value of 4.8±0.2, besides the carbonyl content has value of 24±3 μmol/g indicating that the paper is heavily oxidized.

SEC allowed determining the average value of degree of polymerization, 481(3). This very low value[141] is consistent with a shorter fiber length of the cellulose from wood and with the detrimental effect of acid hydrolysis and/or oxidative cleavage of the cellulose chain during the wood pulping process.

The above results indicate a poor state of conservation of the book thus confirming the problems connected with papers produced by modern papermaking industries. Chemical instability of raw materials causes acidification and strong oxidation of the resulting paper with intense yellowing of the surfaces and brittleness of the folios.

[141] Hubbell, C. A., and Ragauskas, A. J. "Effect of acid-chlorite delignification on cellulose degree of polymerization." Bioresource Technology 101.19 (2010): 7410-7415.

## 5.3 Application of new system of deacidification or simultaneous deacidification reduction and evaluation of efficiency

The investigation survey undertaken on the three cases studies, further confirms that the issue of conservation cannot be faced with general and common procedures. In fact, every artefact has his own history and, as a consequence of the raw materials used for their production, of the inks used to write or print them, on the conservation environment, each one had developed peculiar problems that have to be treated properly in order to guarantee the success of a restoration intervention as well as its long lasting efficacy. For these reasons, it has been decided to subject the three case studies to the following treatments:

- The Archive document belonging to Archivio Storico Diocesano of Palermo (Italy), only deacidification with the nanoparticle dispersion prepared by insolubilisation-precipitation method and described in chapter III.
- The four Gospels in Arabic and Latin belonging to Biblioteca Alagoniana of Syracusae (Italy), simultaneous deacidification – reduction with the system developed and described in chapter IV
- The Breviary of 19th century belonging to a private collection, deacidification with the nanoparticle dispersion prepared by insolubilisation-precipitation method and described in chapter III and simultaneous deacidification – reduction with the system developed and described in chapter IV.

In order to assess their efficacy on real case, each treatment has been compared with the usual method used by restorers.

In the following the application methods are described. Moreover, the efficacy of treatments is evaluated by means of several techniques.

***The Archive document belonging to Archivio Storico Diocesano of Palermo (Italy).***

The restoring procedure adopted by restorers on this document was the following: each bifolio has been preliminarily brushed to remove dust and dirt. This procedure was not considered sufficient to efficient removal. Therefore each bifolio has been washed with deionized water.

The bifolio 14-23 washed with deionized water has been used as reference. pH measurements were carried out on the bifolio after 24 h, 30 days and one year from the above procedure. The pH values of bifolio 14-23 (only washed) are reported in table 5.2.

The pH decreases over time after the washing treatment and indicates that the alkaline compounds are removed by the water. However, it reaches a constant value after 30 days that last up to 1 year.

On the basis of the above result, even if the paper presented a low acidity, it has been decided to apply the deacidification procedure in order to restore the alkaline reserve lost during the washing preliminary to the restoration work. This will allow preventing the browning and ensuring an alkaline buffer against further acids action.

Most of the pages of the document have been deacidified by means of the traditional method[66], i.e. each bifolio has been washed in deionized water and then soaked for 1 h in an aqueous solution of calcium hydroxide (1 g/L).

In order to test the nanolime dispersion obtained by using the insolubilisation-precipitation method, the bifolios 26/35 – 29/32 and 79/88 have been deacidified by using the nanolime dispersion C whose composition is reported in table 3.1. It has been applied following the above procedure: washing in deionized water followed by the soaking for 1 h in nanolime dispersion. The pH measurements have been performed after 24 h, 30 days and 1 year from the two treatments. The pH values acquired on bifolios 39/46, 56/65 and 67/78 after the deacidification with the traditional method (calcium hydroxide concentration = 1 g/L) and on bifolios 26/35 – 29/32 and 79/88 with the nanolime dispersion (calcium hydroxide concentration = 0.1 g/L), are reported in table 5.2.

**Table 5.2.** pH values acquired on various bifolios before and after washing with deionized water and after the deacidification (24 h, 30 days and 1 year).

| Page | Analysed zone | pH before | pH 24h | pH 30 days | pH 1 year |
|---|---|---|---|---|---|
| **Washing with deionised water** | | | | | |
| **14 (verso)** | Unwritten | 8.6±0.3 | 8.1±0.3 | 7.4±0.2 | 7.2±0.2 |
| **23 (recto)** | Inked zone | 6.8±0.3 | 6.5±0.3 | 6.2±0.2 | 6.1±0.3 |
| **Deacidification with the Traditional method** | | | | | |
| **56 (recto)** | Unwritten | 7.1±0.4 | 8.0±0.3 | 6.8±0.2 | 7.4±0.3 |
| **78 (verso)** | Inked zone | 7.3±0.3 | 7.7±0.3 | 7.2±0.3 | 6.9±0.2 |
| **46 (verso)** | Inked zone | 6.4±0.2 | 7.0±0.3 | 7.2±0.4 | 6.9±0.2 |
| **Deacidification with the nanolime dispersion** | | | | | |
| **88 (verso)** | Unwritten | 8.2±0.2 | 8.7±0.3 | 8.0±0.3 | 8.2±0.3 |
| **35 (recto)** | Inked zone | 6.6±0.2 | 8.4±0.4 | 7.4±0.2 | 7.4±0.2 |
| **29 (recto)** | Inked zone | 6.2±0.2 | 8.6±0.2 | 6.8±0.3 | 7.0±0.3 |

The deacidifying effect is more marked in the bifolios treated with nanolime dispersion, even if the amount of calcium hydroxide is 10 times lower than that of the traditional bath. The observed pH trend is similar to that observed for only washed paper but the measured values are still higher than those of untreated paper (only washed). The effect is more relevant on the inked areas. After 1 year the values are unvaried thus indicating that the treatment was effective in establishing an alkaline buffer against acidification.

This result, on the basis of literature findings on similar systems, can be attributed to the nanoparticles entrapment inside the cellulose fibres[142,143,144,145]. The obtained results clearly indicate that the nanolime dispersions obtained by the insolubilisation-precipitation method can be successfully used for the deacidification of paper.

[142] Li, D., He, Q., Cui, Y., Wang, K., Zhang, X., & Li, J.. Thermosensitive copolymer networks modify gold nanoparticles for nanocomposite entrapment. Chemistry–A European Journal, 13.8 (2007): 2224-2229.
[143] Cui, Y., Tao, C., Tian, Y., He, Q., & Li, J.. Synthesis of PNIPAM-co-MBAA copolymer nanotubes with composite control. Langmuir, 22.19 (2006): 8205-8208.
[144] Li, D., He, Q., & Li, J.. Smart core/shell nanocomposites: intelligent polymers modified gold nanoparticles. Advances in colloid and interface science, 149.1 (2009): 28-38.
[145] Li, D., He, Q., Cui, Y., & Li, J.. Fabrication of pH-responsive nanocomposites of gold nanoparticles/poly (4-vinylpyridine). Chemistry of materials, 19.3 (2007): 412-417.

***The four Gospels in Arabic and Latin belonging to Biblioteca Alagoniana of Syracusae (Italy)***

Once known the state of conservation of paper of Four Gospels, some bifolios have been treated by following the procedure described in chapter IV. The restoring procedure adopted by restorers on this document was the traditional deacidification-reduction method prescribed by ICPL[66] i.e. pages have been washed in deionized water and then soaked for 1 h in a calcium propionate (3,5g/l) and TBAB (7g/l) water:2-propanol 1:10 solution.

The applied treatments are summarized in table 5.3.

A sample, labelled as B1, was not treated and it was used as a reference. As a comparison, a sample (B2) was washed in deionized water and soaked in a mixture of water and 2-propanol, 1:10. This mixture is the solvent of the nanolime + TBAB system. A third sample (B3) was treated following the deacidification-reduction treatment used by ICPL. Finally, the sample B4 was washed in deionized water and then soaked in nanolime-TBAB dispersion for 1 h.

**Table 5.3:** Schematic representation of treated paper samples**.**

| Samples | Treatments |
|---|---|
| **B1** | Reference untreated |
| **B2** | Water:2-propanol 1:10 solution |
| **B3** | Calcium Propionate C=3,5g/l + TBAB C=7g/l<br>in water:2-propanol 1:10 solution (literature method) |
| **B4** | Nanolime C=0.05%w/w + TBAB C=7g/l<br>in water:2-propanol 1:10 solution (innovative method) |

A first evaluation of the efficacy of the treatment has been obtained by surface pH measurements repeated at 24 h and 30 days after the treatment. The pH values are reported in table 5.4.

The pH of the reference bifolio (sample B1) remains unchanged as expected. Washing sample B2 induces a slight increase of pH probably due to the removal of soluble acidic compounds from the paper. The deacidification-reduction method induces a strong increase of the pH that becomes alkaline with a value falling within the optimum pH range. Let us note that the pH values for the

samples treated with the method proposed here were slightly higher than those measured on the samples treated with the literature method.

With the aim to evaluate a possible improvement of molecular characteristics of cellulose, $^{13}C$ {$^{1}H$} CP MAS NMR spectra were acquired on the treated samples. For the analysed samples no significant variation has been observed. The attribution of all peaks has been performed as described above. Both the crystallinity degree (55%) and oligomers presence are almost coincident with those of the reference B1 sample. The area of the carbonyl peak slightly decreases from sample B1 to B4 thus suggesting a reduction of the carbonyl content. Due to the low signal to noise ratio, a quantitative evaluation is meaningless and for this reason FT-IR spectra have been acquired. The region of the FT-IR spectra where the ν(C=O) stretching falls is shown in figure 5.10. The R ratio was calculated for all samples as previously described (page 63) and its value is reported in table 5.4.

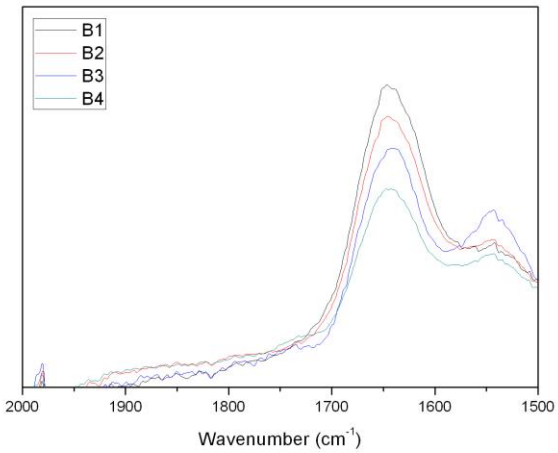


**Figure 5.10.** FT-IR spectra. The range from 1500 $cm^{-1}$ to 2000 $cm^{-1}$ has been selected to evidence the variation underwent by the ν(C=O) peaks.

**Table 5.4.** pH values and R ratio of ancient samples. R is the ratio between the area of the carbonyl peak (1730 $cm^{-1}$) and that of CH stretching (2850-2950 $cm^{-1}$). DP is the degree of polymerization. The mean pH value before treatment is 5.5±0.4 evaluated on several point of 15 bifolios.

| Sample | pH 24 h | pH 30 days | R | DP |
|---|---|---|---|---|
| **B1** | 5.1±0.1 | 5.1±0.1 | 6.4 | 1080 (40) |
| **B2** | 5.6±0.1 | 6.0±0.1 | 4.3 | 1200 (100) |
| **B3** | 8.7±0.1 | 8.6±0.1 | 4.1 | 1140 (70) |
| **B4** | 8.5±0.1 | 9.2±0.1 | 2.7 | 1350 (40) |

The R ratio value decreases from B1 to B4 sample thus demonstrating the efficacy of the treatment in reducing the carbonyl content in the paper. It is worth noticing that while the literature method induces a reduction of about 35% of carbonyl content[146] the new treatment proposed here has been evidenced to be more effective by reducing the carbonyl content up to 58%. These results can be useful to explain the changes in pH values. In fact the alkaline pH value noted for the treated sample can be ascribed to a decrease of the acidic (carboxylic) groups number within the cellulose chains is measured by FTIR. As a consequence it can be assumed that the autocatalytic degradation

[146] Capitani, D. et al. "Ancient deteriorated paper: washing and restoring processes as studied by $^{13}C$ CP-MAS NMR spectroscopy." Quinio 2 (2000): 37-43.

through acid assisted hydrolysis of glycosidic bonds is ceased or the reaction proceed slowly via other mechanisms.

On the basis of results obtained for the laboratory specimens already described in chapter IV, we expected a variation of DP based on crosslinking among cellulose chains. To deepen this aspect, SEC method was applied and the values of degree of polymerization are reported in table 5.4.

Results are in fairly good agreement with those obtained from the investigation on the laboratory specimens. Sample B2 and sample B3 maintain, within the experimental error, the same degree of polymerization of cellulose as that obtained for the untreated paper (sample B1). The proposed treatment instead promotes the formation of crosslinking between cellulose chains thus inducing an increase of the degree of polymerization (sample B4). This could be ascribed to a synergic effect of nanolime and TBAB. In fact, the nanolime weakly positively charged[97] interacts with the negatively charged oxycellulose. This interaction strengthens the one occurring among the tert-butyl ammonium and oxycellulose thus favoring the crosslinking among chains.

The color difference has been measured by evaluating the color difference ΔE(CIE76) and values are reported in figure 5.11.

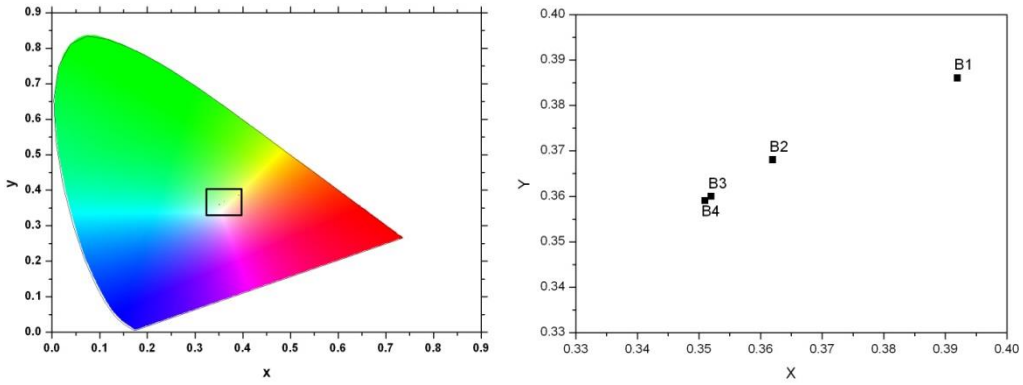


**Figure 5.11.** Reflectance measures in the relative CIE 1931 color space. On the right: enlarged view of the area highlighted by rectangle.

Reference sample (B1) is far from the white point (axes intersection of enlarged plot). The washing with the mixture water:2-propanol 1:10 improves the color of the paper probably by solubilizing some chromophores from the degraded paper[147]. Both the treated samples, B3 and B4, are closer to the white point. Anyway, the treatment developed in this study demonstrates to be more effective than that based on calcium propionate with TBAB even with respect to optical properties of paper.

[147] Conte, A. M., Pulci, O., Knapik, A., Bagniuk, J., Del Sole, R., Lojewska, J., & Missori, M. Role of cellulose oxidation in the yellowing of ancient paper. Physical review letters, 108.15 (2012): 158301.

***The Breviary of 19th century belongs to a private collection.***

The Breviary, up to now, has not been subjected to a restoration intervention. In order to assess the efficiency of the new developed methods in a real case of lignin paper, it was decided to test both, the deacidification treatment with nanolime and the simultaneous deacidification reduction treatment with nanolime and TBAB. Some pages, chosen accounting for their homogeneity of pH values, have been carefully taken off from the book and two of them have been treated by applying the two systems. In order to evaluate the efficiency of treatments, two pages have been treated with the traditional deacidification method and the traditional deacidification-reduction method prescribed by "Istituto Centrale per la Patologia del Libro" (ICPL)[66], respectively. Moreover, one page has been left as it was and one has been washed with the solvent and both used as references.

The applied treatments are summarized in table 5.5.

**Table 5.5:** Schematic representation of treated paper samples.

| Pages | Treatments |
|---|---|
| **A1** | Reference untreated |
| **A2** | Water:2-propanol 1:10 |
| **A3** | Calcium Propionate C=3,5g/l (Literature method[66]) |
| **A4** | Nanolime C=0.05%w/w (Innovative method) |
| **A5** | Calcium Propionate C=3,5g/l + TBAB C=7g/l in water: 2-propanol 1:10 solution (Literature method[66]) |
| **A6** | Nanolime C=0.05%w/w + TBAB C=7g/l in water:2-propanol 1:10 solution (Innovative method) |

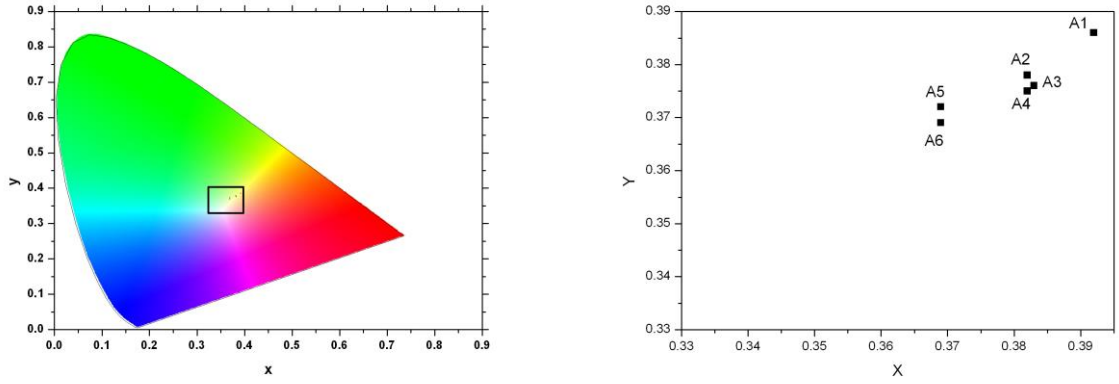


**Figure 5.12.** Reflectance measures in the relative CIE 1931 color space. On the right: enlarged view of the area highlighted by rectangle, the axes intersection represents the white point.

**Table 5.6.** pH values, Carbonyl content and DP of Breviary samples. DP is the degree of polymerization. The mean pH value before treatment is 4.8(2) evaluated on several point.

| Sample | pH 24 h | pH 30 days | pH 90 days | pH 120 days | Carbonyl content (µmol/g) | DP |
|---|---|---|---|---|---|---|
| **A1** | 4.8(2) | | | | 24 (3) | 481(3) |
| **A2** | 6.0(1) | 6.1(1) | 5.7(1) | 5.4(1) | 23 (3) | 400(10) |
| **A3** | 7.2(2) | 7.1(1) | 7.3(1) | 7.2(1) | 23 (3) | 436 (2) |
| **A4** | 8.3(1) | 8.3(1) | 8.2(1) | 8.0(1) | 25 (3) | 460 (5) |
| **A5** | 8.6(1) | 8.1(1) | 8.0(1) | 7.7(1) | 8 (1) | 504(1) |
| **A6** | 9.1 (2) | 8.7(1) | 8.1(1) | 8.1(1) | 4 (1) | 454 (1) |

The pH of the reference sample A2 increases as a consequence of an efficient removal of acid residues with respect to the unwashed sample A1. Its value slightly decreases with time thus indicating that the degradative processes are still ongoing. The deacidification treatment with the literature method[66] is able to bring the pH value within the optimum pH region and the treatment exerts its action up to 120 days. The deacidification treatment with the nanolime suspension is able to buffer pH value within the optimum pH region but the measured pH is higher with respect to the A3 sample thus indicating the ability of nanolime to produce an alkaline reserve. The literature deacidification reduction treatment[66] reveals to be more efficient in increasing pH with respect of both the two previous deacidification treatments but it is not able to buffer the pH during the natural aging. The same happens for A6 sample even if the absolute pH value is higher as compared to A5 sample.

In order to have a better understanding on the efficiency of the new deacidification reduction method, the aldehyde and ketone carbonyl content values was determined by the Szabolcs methodology[85]. This methodology is more selective than the FT-IR spectroscopy despite being a destructive methodology. Values are shown in table 5.6. The measure clearly assess the efficiency of the innovative system: the traditional method gives paper with an acceptable results within optimum carbonyl content region (below 8 µmol/g) instead the innovative method produces an even lower value, 6 times lower than the reference one.

SEC method was applied on treated samples and the values of degree of polymerization are reported in table 5.6. The results showed a trend in line with that found on the P3 specimens, in fact the difference among DP values for treated and untreated samples is below 10%.

This finding suggests that lignin play a significant role probably as consequence of specific interactions with cellulose.

The goodness of the treatment is confirmed also by the colorimetry. In fact ΔE(CIE76) values showed in figure 5.12 indicate that the sample A6 is the nearest to the white point thus indicating that the treatment is able to improve the optical properties of the paper.

# *Conclusion*

To quote Quaglierini and Amorosi in *Chimica e tecnologia dei materiali per l'arte*[148] **"**The first source of degradation of an artwork lies in the artwork itself and, in particular, in its material composition; in the best case our conservation intervention will only slow this degradation".

The modern conception of restoration aims to understand the causes lying at the basis of material degradation and to foresee proper intervention able to slow down the ongoing processes.

In the past decades the interests of researchers have been devoted to the development of new materials and procedure able to prevent further degradation of artwork. The echo on specialized journals had become growing since the news of Phillip Ball on Nature[149]. In that news the author said, "Had Leonardo da Vinci known about nanotechnology, his Last Supper might not be in its present sorry state. [….] Leonardo was no chemist".

During my PhD research, two systems designed for restoration of paper have been developed and applied on some case studies.

The first system is based on diluted nanolime suspension able to deacidify paper. An innovative way, the insolubilisation-precipitation method, for the production of nanolime has been introduced. The method is shown as an innovative, economic and one-step route for the preparation of nanolime dispersion. The dispersion was obtained adding the 2-propanol in an aqueous solution of bulk $Ca(OH)_2$ under inert atmosphere. Nanoparticles dispersed in a water/2-propanol mixture were obtained without any manipulation of the dispersion. The synthesis was performed at different alcohol content (20, 50, 90 vol.%) and at different temperatures (40, 60 and 76 °C), in order to understand the role of alcohol amount or mixture composition and of temperature on the kinetic stability of the dispersions and on the morphology of the nanoparticles. The stability of the dispersion together with particle size and morphology were found to be dependent on water to 2-propanol molar ratio and on the temperature.

The second is an innovative system for simultaneous deacidification and reduction of paper composed of nanolime dispersion in a hydro-alcoholic solution of TBAB. The nanolime has been

[148] Quaglierini, C., and Amorosi, L. Chimica e tecnologia dei materiali per l'arte. Zanichelli, 1991.
[149] Ball, P., "Nanotechnology restores flaking frescos" Nature, 2001
http://www.nature.com/news/2001/010712/full/news010712-8.html

prepared by the insolubilisation – precipitation method. Moreover, a proper protocol of application has been set. The treatment utilizes simple immersion of paper in a 2-propanol solution of TBAB and nanolime in a single fast step. It reveals to be very efficient to improve the mechanical resistance and inhibits both oxidation and acidic hydrolysis of paper. It is effective in reducing both acidity and the carbonyl content of samples highly degraded. From the perspective of paper conservators, the procedure stabilizes the pH within the optimum region during the artificial aging. In addition, it reveals to be able to maintain the degree of oxidation after artificial aging at a value comparable or better of the reference and, in case of cellulose paper, promotes a crosslinking or branching of cellulose chains that continues during artificial aging and has a protective effect also against aging induced by light radiation.

Once set the efficacy of the second method on specimens chemically oxidized and artificially aged, both systems were tested on real cases.

The application of the nanolime dispersion having the better structural and mechanical properties to the deacidification of a document of the *Gran Corte Arcivescovile di Palermo* and of a *Breviary of 19th century*, was followed by pH measures that indicate the efficiency of nanolime in stabilizing the pH values and restoring alkaline reserve in case of cellulose paper made by rags and lignin paper made by wood pulp.

The treatment for simultaneous deacidification and reduction was tested to *a 16th century four gospels book* and on the *Breviary of 19th century*. Results were very promising in terms of chemical, optical and mechanical properties. In particular for both cases, the cellulose oxidation modified the durability of the paper and its colour. After reduction, an increase in stability and resistance of the paper was obtained and, as a positive side effect, the removal of the yellowing with improving reading possibility. The treatment produces whitened paper with desired pH values in this way by supressing hydrolytic degradation and cellulosic chain scission and reduces the oxidation degree. It, in case of cellulose paper, has also been demonstrated to give rise to a significant improvement of mechanical properties by promoting an increase of polymerization degree. The long lasting efficiency of the proposed treatment was evaluated by artificial aging of treated specimens. The overall results indicate that the new proposed treatment, able to protect cellulose paper from further degradation process, is able to exert its action for long aging time and it reveals to be more effective than similar treatments already applied by restorers.

The investigation survey and the tests undertaken on the three cases studies, further confirms that the issue of conservation cannot be faced with general and common procedures. In fact, every

artwork has his own history and, as a consequence of the raw materials used for their production, of the inks used to write or print them, on the conservation environment, each one had developed peculiar problems that have to be treated properly in order to guarantee the success of a restoration intervention as well as its long lasting efficacy.

# *APPENDIX*

## *INSTRUMENTATION AND ANALYSIS PROTOCOLS*

UV-Vis spectra were recorded in the range 200-800 nm with resolution of 1.0 nm using a double beam Beckman DU-800 spectrophotometer. The absorbance values selected are those at 600 nm in correspondence of which the absorbance of species in suspension is negligible. ξ value ranges from 0 (complete sedimentation, unstable dispersion) to 1 (no settling of the particles, perfect kinetic stability of the dispersion).

The UV-Vis Diffuse Reflectance measurements were conducted with a spectrometer Ocean Optic DHmini USB2000 by choosing CIE Chromaticity *coordinates (x, y, z) color space* with illumination source D65. The color difference from the standard white has been measured by evaluating the color difference ΔE calculated by means of the equation according to CIELab model:

$$\Delta E = \sqrt{(x_P - 0.333)^2 + (y_P - 0.333)^2 + (z_P - 0.333)^2}$$

where ΔE is total color change for expressing discoloration of the paper in comparison to the white and $x_p, y_p, z_p$ are the measured colorimetric coordinates of the paper samples.

The effect of UV-Vis radiation was tested using a microfadeometer apparatus that comprises of a high-powered continuous-wave xenon light source (Ocean Optics HPX2000) and a UV-Vis spectrometer (Avantes Avaspec 2048) coupled to a 0◦/45◦ geometry optical probe head by a solarisation resistant optical fibre with a 600 micron fibre core.[150, 151]

Dynamic light scattering (DLS) measurements were performed at 90° using a Brookhaven instrument equipped with a BI-9000AT digital autocorrelator, a He–Ne 632.8 nm laser source working at a power of 75 mW and a photomultiplier tube detector. Data were obtained in the form of electric field self-correlation function, C(τ), as function of the decay time, τ, using the software supplied by Brookhaven Inc.

[150] Łojewski, T., et al. "Note: Light ageing with simultaneous colorimetry via fibre optics reflection spectrometry." Review of Scientific Instruments 82.7 (2011): 076102.
[151] Lerwill, A., et al. "A portable micro-fading spectrometer for versatile lightfastness testing." E-Preservation Science 5 (2008): 17-28.

Transmission Electron Microscopy (TEM) micrographs were acquired by using a JEM-2100 (Jeol, Japan) operating a 200 kV accelerating voltage, equipped with an energy dispersive X-ray spectrometer (EDS, Oxford, UK) suitable for element identification. A drop of each dispersion was deposited on a 300 mesh lacey-carbon grid and the solvent was let to evaporate completely before the analysis. The crystalline phase was identified by means of Selected Area Electron Diffraction (SAED) technique. SAED patterns were collected using a CCD camera (Gatan MSC KAF1000).

Raman spectra were acquired through a Renishaw inVia Raman Microscope spectrometer equipped with a microprobe (50 ×) and a CCD detector with a Nd:YAG laser (532 nm).

The degree of polymerization of the papers was measured using Size Exclusion Chromatography following the Pawcenis et al.[152] method, by means of a Waters chromatographic system which consists of an isocratic pump 1515, an autosampler 717+, a column oven, a multiple angle laser light scattering (MALLS) detector (Dawn Heleos, Wyatt Technology, working at 658 nm) and a differential refractive index detector (Optilab T-rEX, Wyatt Technology, working at 658 nm) acting as a concentration sensitive detector. Separation was performed with the use of a set of two 25 cm × 1 cm mixed-bed polydivinylbenzene columns (Jordi) thermostated at 35 °C. THF (HPLC grade, J. T. Baker) was used as an eluent with a flow rate of 1.0 $cm^3$/min. Astra 6.1.1.17 (Wyatt Technology) software was used to process and analyze chromatographic and MALLS data. Molar mass and degree of polymerisation (DP) values were averaged from 8 measurements: 4 injections from 2 separate batches of paper.

$^{13}C$ {$^{1}H$} CP MAS NMR spectra were obtained at room temperature with a Bruker Avance II 400 MHz (9.4 T) spectrometer operating at 100.63 MHz for the $^{13}C$ nucleus. 1800 scans were collected with spinning rate of 5 kHz, a contact time of 1.5 ms and a repetition delay of 2 sec. The Hartmann-Hahn condition[153] was optimized on adamantane sample which was also used as the external reference. Samples were placed in 4 mm zirconia rotors and sealed with KEL-F caps using silica as a filler to avoid inhomogeneities inside the rotor. Paper sampling necessary for NMR analysis, was carried out to minimally damage the artefact by taking a small stripe (c.a. 10 mg) of the upper edge of the sheet.

FT-IR spectra were acquired with a VERTEX 70v spectrometer, BRUKER. Spectra were collected in transmission mode using thinned samples and reduced pressure environment (0,002 atm) for

[152] Pawcenis, D., et al. "Towards determination of absolute molar mass of cellulose polymer by size exclusion chromatography with mulitple angle laser light scattering detection." Journal of Chromatography A 1409 (2015): 53-59.
[153] Hartmann, S. R., Hahn, E. L. Nuclear double resonance in the rotating frame. Physical Review, 128.5(1962): 2042.

suppressing the effects of water vapour. By exposing a sample to vacuum for several minutes the bound water included in paper whose bending vibrations appear at around 1640 $cm^{-1}$ can be desorbed[140]. Each measurement was acquired in the spectral range 4000-400 $cm^{-1}$, with an average spectral resolution of 2 $cm^{-1}$. 60 scans were acquired for each sample. Prior to the transmission FTIR in situ measurements the thinned samples of aged paper were prepared by mechanical scratching of the paper surface.

pH measurements were carried out with an HANNA Instruments pH-meter pH211 equipped with a flat electrode HI1413 according to the TAPPI method[154], [155].

The oxidation of cellulose was evaluated by determining the carbonyl content paper accordingly to the Szabolcs methodology[85]. The 2,3,5-Triphenyltetrazolinium chloride (TTC) compound forms a colorless solution when dissolved in water. After reaction with carbonyl, a red insoluble compound is formed. The redox reaction is quantitative. The precipitate was separated from the aqueous phase and dissolved in ethanol. The absorbance of the resulting solution was measured at 546 nm by an UV-VIS Bechman DU800 spectrophotometer. The carbonyl content was evaluated by interpolation via a calibration curve that was built by oxidation of known concentration of glucose.

Zero span tensile strength was measured according to the TAPPI standard T231 om-85 Zero Span-Breaking Strength of Pulp (Dry Zero Span Tensile) on the Pulmac Troubleshooter TS-100 instrument. The measured pressure, read out from the device, was recalculated into the force and then into the breaking length. For each sample this property was measured 20 times. The tensile strength was measured at zero span. The tensile force is calculated per unit area of sample and therefore generally quoted as 'pressure'. The pressure to break at zero gap, failure load, is calculated from

$$\text{failure load} = K(P - P_O)$$

where K is the instrument constant (0.422kg/psi), P is the observed pressure at break (psi), and Po is the 'zero' pressure (psi) required to overcome the zero load which maintains the jaws in contact at any given time.

The breaking length is calculated as:

$$\text{breaking length (km)} = \text{failure load} / \text{width (m)} * \text{grammage } (g/m^2)$$

[154] T 529 om-04 Surface pH measurement of paper
[155] Ray, C.T. “Flat Electrode Measurement of pH in Printing Papers”, Tappi, 55.3 (1972):393-395.

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## *Curriculum Vitae*

**Education:**

**September - December 2015.** Research period at Jajellonian University, Kracow, Poland, under the supervision of Prof. T. Lojewski on Chemical and physical investigation on cellulose materials treated by innovative conservative methods.

**Workshoop and schools**

Corso di Aggiornamento in "Metodologie Avanzate di Risonanza Magnetica (NMR) per lo Studio dei Beni Culturali", Sala Odeion, Museo dell'Arte Classica, Sapienza Università di Roma, 24 febbraio 2014

Thematic School on Conservation Science Paper Materials: From Diagnosis to Conservation, Izmit, Kocaeli University – Turkey, 17-26 June 2014.

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